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Validation Data For Photochemical Mechanisms

Experimental Results

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16. ABSTRACT

The smog chamber facility of the University of North Carolina (UNC) was used to provide experimental data for the EPA and atmospheric model developers for testing and validating kinetic mechanisms of photochemical smog formation. In this study, 71 dual-experiments were performed using NO_x and various hydrocarbons and hydrocarbon mixtures. Experiments were also conducted to better understand and characterize (1) the chamber when operated dynamically to simulate continuous emissions and dilution, and (2) the solar radiation inside the smog chamber. The chamber experiments described in the report have been added to the existing UNC database for model testing, bringing the total number of dual-experiments in the database to 417. The database is available on an ANSI formatted magnetic tape.

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Abstract

The smog chamber facility of the University of North Carolina (Chapel Hill) was used to provide experimental data for the EPA and atmospheric model developers for testing and validating kinetic mechanisms of photochemical smog formation. These mechanisms are used to calculate needed urban air pollution emissions reductions. Previous research has demonstrated that using different mechanisms in the EKMA procedure results in significantly different predicted hydrocarbon reduction requirements to achieve the desired ozone standard. This is due to inaccurate and incomplete descriptions in some of the mechanisms. However, insufficient validation data were available to determine which mechanisms are incorrect.

In previous research we have produced 346 dual-experiments to aid in the development of chemical mechanisms. In this project, after organizing and analyzing existing experiments for initial model validation, we performed new experiments to: 1) provide "missing" data; 2) resolve differences between the model's predictions and the existing experimental data; 3) extend the range of urban-like conditions in the data base; and 4) aid in model construction and testing as requested by model developers.

The previous experiments were designed for developing chemical mechanisms. These experiments emphasized the chemistry of single hydrocarbons, mixtures of single hydrocarbon classes, the reactivity of different hydrocarbon mixtures including automobile exhaust, and other basic questions of reactivity. Analysis of this experimental set showed the need for experiments with urban-like conditions (complete urban-like hydrocarbon mixtures) to test hydrocarbon control strategies and reactivity issues such as hydrocarbon substitution and the importance of aldehydes. It was also clear that quality assurance efforts for both chemical and physical data (especially characterization of light inside the chamber) would be of greater importance because of refinement of model testing requirements.

The smog chamber, located outdoors in rural North Carolina, is an A-frame structure supporting Teflon film. Because the chamber is partitioned into two sections, each with a large volume of 156 m^3, two experiments can be conducted simultaneously with the same conditions of light, temperature, humidity, and any "chamber background" conditions. The dual chamber is operated under natural conditions of solar radiation, temperature, and relative humidity.

In this study, 71 dual-experiments were performed using NO_x and various hydrocarbons and hydrocarbon mixtures. Many more additional experiments were conducted to better understand and characterize:(1) the chamber when operated dynamically to simulate continuous emissions and meteorological dilution, and (2) the light inside the smog chamber. The smog chamber experiments performed during this two-year project have been added to the existing UNC database for model

validation testing, bringing the total number of dual-experiments to 417. Data processed through our computerized system will be distributed on industry standard magnetic media, complete with detailed guidance documents.

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1

Introduction

Photochemical reaction mechanisms are central components in EPA's models for computing control requirements for organic emissions needed to meet Federal Air Quality Standards for ozone. State and local control officials are expected to use these models to estimate control requirements. Different modelers sometimes apply different methods however, resulting in different descriptions of the same situation. Smog chamber data can be used to test photochemical mechanisms to determine the adequacy of the chemical representation. Previously, mechanism testing had not used a large enough range of test data encompassing the range of conditions likely to occur in an urban control situation. This is in part because testing had been concentrated on the immediate need to study basic chemistry and reactivity issues.

Our previous work had organized the earlier experimental database which presented a hierarchy of experimental complexity and testing.[1] Modeling results and analysis of the existing smog chamber and support data indicated areas where additional research was needed to test more completely chemical mechanisms. For example, experiments with more urban-like conditions to test hydrocarbon control and reactivity effects from hydrocarbon substitution were needed. Experiments were needed to resolve special modeling problems and to answer modelers specific questions. Experiments were needed to test newly implemented features (new species and chemistry) of the newer chemical mechanisms.

Purpose

The purpose of this research project was to: (1) measure reactant and product concentrations as functions of time in selected photochemical smog systems; (2) process these data into a form readily distributable to model developers and testers;

and (3) provide auxiliary information needed to create mathematical model descriptions of the systems. The 71 dual-experiments, when added to the other experiments in the database, encompass a range of complexity from single HC species in totally static situations to complex urban mixtures in fully dynamic conditions. As a whole, the data set is well suited to develop and test models of chemical transformations in polluted atmospheres. To maximize the usefulness of the experimental database, a comprehensive quality assurance description of the data acquisition, processing, and calibration procedures, and the chamber facility is provided elsewhere.[2]

Determination of Research Needs

Provide Missing Data

In the most basic terms, missing data fell into three categories: missing smog chamber experiments, missing information which would aid modelers, and experiments to test new developments in the newer chemical mechanisms. Modelers need to know more about the uncertainties of the data, and about other details of the facilities to help them make necessary assumptions, approximations, or calculations such as treatment of light inside the chamber. The estimated uncertainties in the data determine the degree of agreement which must be attained.

Smog Chamber Experiments

The previous research organized the 346 experiments allowing for assessment of research needs. Figure 1 shows the distribution of the experiments by groups and hydrocarbon. The earlier experiments concentrated on the chemistry of specific compounds and classes. The effect of hydrocarbon control was usually investigated with these simpler experimental systems since these were better understood. Basic reactivity research utilized simple mixtures, and substitution of one major compound into a simple mix. Research proceeded with the use of mixtures of increasing complexity. Figure 1 shows a large number of complex mixture experiments. These followed recomendations from urban atmospheric measurements made in 1975. By the end of 1983 we had performed experiments with automobile exhaust, and with a synthetic hydrocarbon mixture that approximated the reactivity of automobile exhaust. We were also able to generate a synthetic urban-like mixture which matched recent extensive atmospheric measurements. Most experiments using these mixtures compared the reactivity of one mixture versus another. Only a few experiments were performed with these mixtures, to demonstrate the effect of reduced total hydrocarbon (hydrocarbon control)

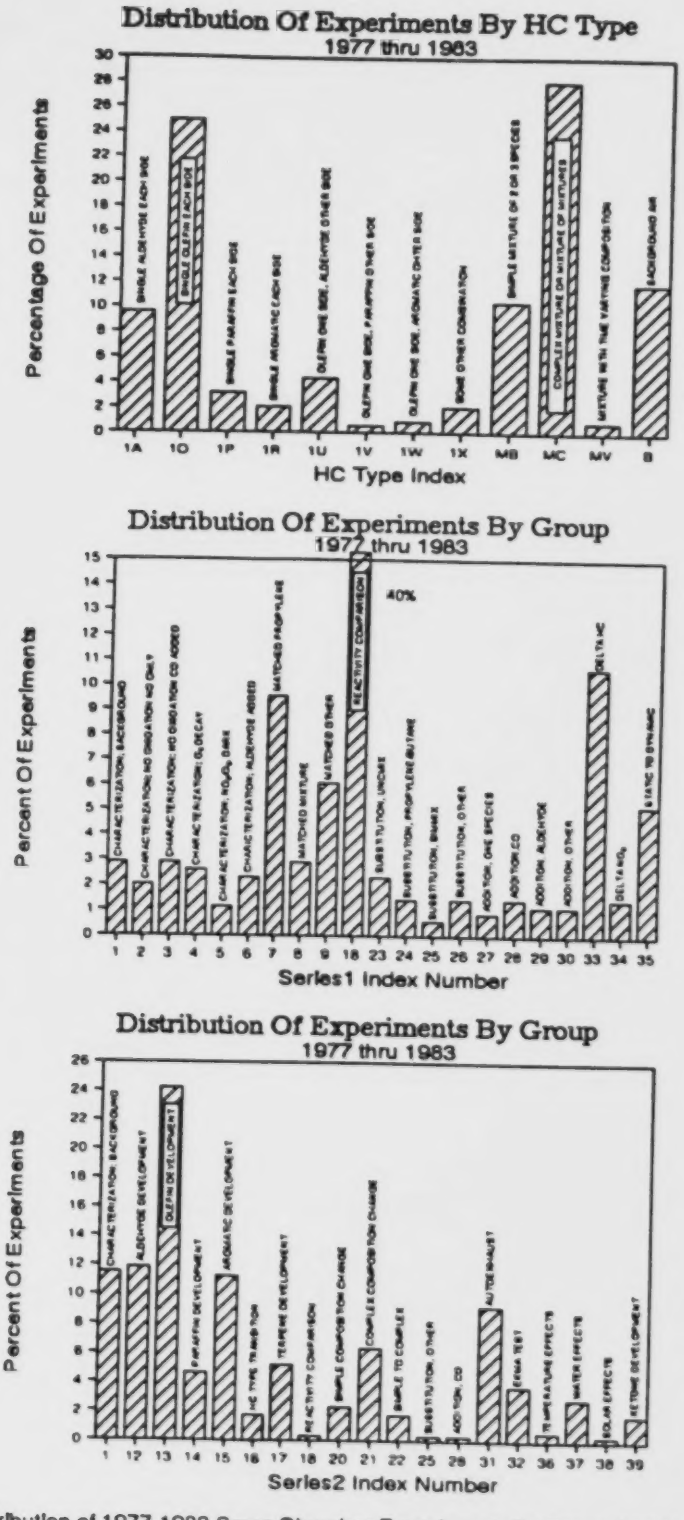

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Figure 1. Distribution of 1977-1983 Smog Chamber Experiments By Group And Hydrocarbon Type.

or other control issues. The effect of substitution of different hydrocarbons into these most urban-like hydrocarbon mixtures or the effects of aldehydes on the reactivity of the mix were clearly needed to more fully test chemical mechanisms.

Data Uncertainty For Modelers - Quality Assurance Details

It was realized that increased documentation of the dataset, including quality assurance, was of primary importance at this stage of chemical mechanism testing. Modelers need to know as much as possible about the uncertainty in the data used for testing. Details of the chamber construction and operation help the modeler decide how to treat chamber artifacts. A detailed description of the facilities, instrumentation, data-acquisition system, calibration sources and traceability to NBS sources, including the measurement of light, and a complete record of calibration for the two years, has been produced.[2] Characteristics of the research site that that possibly affect the solar light inside the chamber were also presented.

Resolve Differences Between Predictions And Data

Modeling studies using different mechanisms indicated that problems were encountered in modeling complex mixtures containing aromatics and, surprisingly, mixtures containing large fractions of ethylene, and ethylene itself. Chemical mechanisms did not simulate the reactivity changes occuring when the HC-to-NO_x ratio was varied. Problems were not restricted to one chemical mechanism. The experiments designed to extend the range of urban conditions, and those to address aromatic reactivity all help to solve these general problems between prediction success. Many experiments conducted to assist modelers (see below) were also used to resolve differences between mechanisms.

For the ethylene experiments conducted at low and high HC-to-NO_x ratios, the simulations required large variations in assumptions of chamber background sources of HONO and HCHO in order to fit the data. Even the experiments conducted at mid-range ratios required significant radical sources (HONO) to adjust initial timing. No HONO was needed to adjust timing of high ratio ethylene runs, and very large amounts of HONO and HCHO were needed to model low HC-to-NO_x ratio ethylene experiments. Additional ethylene experiments were conducted where special analytical techniques were utilized to help modelers resolve the ethylene reactivity problem. These are discussed in another section where these special analytical measurements are presented.

Similarly, there appeared to be less success in modeling experiments with large fractions of aromatics. At the beginning of this project, mechanisms such as

the Carbon Bond III contained only one aromatic species that was used to represent the different chemistries of toluene and other aromatics. This was done by adjusting chemistry for a "representative" urban hydrocarbon composition. The Atkinson, Lloyd, and Winges (ALW) mechanism, the Carbon Bond IV (CB4) and the Carter, Aktinson, Lurman, and Lloyd (CALL) mechanism, with two or more aromatic species for toluene, xylene and trimethylbenzene type aromatics were designed to correct this limitation to better simulate complex hydrocarbon mixture composition variation. Even the ALW mechanism, however, had difficulty with simulations since the details of aromatic chemistry is not well understood. Thus, experiments were needed to test the chemistry of aromatics further.

Extending The Range of Urban-Like Conditions

As described above, experiments were needed to extend the range of urban-like conditions. That is, experiments needed to be conducted with reasonably complex hydrocarbon mixtures based on automobile and atmospheric compositional data. The experimental design for this study utilized the dual-nature of the smog chamber. Some experiments used the same mixture on both sides and only the amount of initial hydrocarbon was varied. This resulted in two experiments with the same light and physical conditions for modelers to test a mechanism's ability to predict ozone from two levels of initial hydrocarbon (a situation which is needed to successfully and accurately predict control requirements). Other experiments that utilized the dual-nature of the smog chamber system included injecting different amounts of the same complex mixture into each side of the chamber. Substitution effects in complex mixtures were investigated by adding another species or mixture to the lower hydrocarbon side to make the total equal on both sides. Similarly, the effect of aldehyde composition in complex mixtures was studied.

Assistance to Model Developers

Modelers from various groups suggested additional experiments be conducted to aid in their work. Some of these were special "characterization" types, such as testing photolysis rates of ozone and formaldehyde, and strengths of radical sources and NO_x wall sources. Several groups suggested hydrogen peroxide and formaldehyde experiments. The specific, sensitive,tunable diode laser system of Unisearch Inc., which was used at the UNC smog chamber, allowed us to conduct experiments with these compounds.

Solar irradiance, at the research site and inside the chamber was investigated in more detail than before. The absolute calibration factors of the Eppley ra-

diometers were investigated, including tracing back to NBS standards. The structural effects of the chamber and surrounding buildings and trees were studied.

Additional investigations to understand and represent conditions in the dynamic experiments that used continuous emissions and dilution were undertaken. These included experimental flow mapping inside the chamber, and modeling of the original experiments' tracer data.

Research Products

Results are data and information which will assist those involved in continuing efforts to 1) develop and validate photochemical models and 2) understand the relationships and importance of ozone precursors and factors which result in ozone in the urban troposphere.

2

Provide Missing Data

Smog Chamber Experiments

Experiments were designed and conducted to fill gaps in previous research. Toluene and other important aromatics had been studied extensively in earlier experimental programs, but usually in simple mixes to demonstrate the differences among aromatics in mixtures with reasonable representation of the different HC classes. It was realized from analyzing the organized set of 346 experiments that there was a need for experiments comparing single aromatics against each other, and in the more complex, most recent urban-like mixtures. Several of these experiments were conducted and a sample set is listed in Table 1. The experiments conducted with the more-urban-like mixtures are listed and discussed in a later chapter of this report.

Discussion Of Results From Example Experiments

Two experiments of particular interest were comparisons of the reactivity of toluene versus m-xylene, and m-xylene with o-xylene. The experiment comparing 5.0 ppmC of toluene with 2.0 ppmC of m-xylene was conducted with the same NO_x on each side. The NO_x and O_3 results of June 27, 1984 are shown in Figure 2. The $HO^{\cdot}$ rates are significantly different for these two aromatics. This experiment also shows other differences including the different O_3 yields of these compounds.

This dual experiment was modeled with the CB4.1 chemical mechanism. Remarkably, the NO_x and O_3 profiles are simulated very well on the m-xylene side and fairly well on the toluene side: although ozone is overpredicted by about 75 ppb (see Figure 3). The two systems produce largely different amounts of PAN. The m-xylene side produced almost 7 times more PAN than the toluene side which

Table 1. "Missing Experiments" Conducted

Date	CDI	HC	Ser	Proj	Q	I	P	Sun	Rank
25-Jun-84	ONI	1R	18	ET	3	8	P	88	Best of kind
	Red Side	0.800	NOx	3.00	M-XYLENE				
	Blue Side	0.800	NOx	3.00	TOLUENE				
26-Jun-84	ONI	1R	18	ET	8	8	P	99	Best of kind
	Red Side	0.500	NOx	2.80	O-XYLENE				
	Blue Side	0.500	NOx	3.00	M-XYLENE				
27-Jun-84	ONI	1R	18	ET	8	8	P	81	Best of kind
	Red Side	0.344	NOx	1.99	M-XYLENE				
	Blue Side	0.335	NOx	4.91	TOLUENE				
28-Jun-84	ONI	1R	18	ET	7	7	P	47	Best of kind
	Red Side	0.500	NOx	3.00	M-XYLENE				
	Blue Side	0.500	NOx	6.00	TOLUENE				
12-Aug-85	ONI	MC	23	ET	7	6	P	43	Satisfactory
	Red Side	0.350	NOx	2.10	UNCMIX				
				0.90	M-XYLENE				
	Blue Side	0.350	NOx	2.10	UNCMIX				
				0.90	1,2,4-TRIMETHYLBENZENE				
15-Aug-85	ONI	MC	23	ET	8	9	P	92	Satisfactory
	Red Side	0.350	NOx	0.90	M-XYLENE				
				2.10	UNCMIX				
	Blue Side	0.350	NOx	0.90	1,2,4-TRIMETHYLBENZENE				
				2.10	UNCMIX				

Table 1. cont. "Missing Experiments" Conducted

Date	CDI	HC	Ser	Proj	Q	I	P	Sun	Rank
21-Jun-85	ONI	1A	33	ET	5	6	P	91	Best of kind
	Red Side	0.350	NOx	1.50	FORMALDEHYDE				
	Blue Side	0.390	NOx	0.75	FORMALDEHYDE				
10-Jul-85	ONI	1A	33	ET	8	9	P	81	Satisfactory
	Red Side	0.500	NOx	1.50	FORMALDEHYDE				
	Blue Side	0.500	NOx	0.75	FORMALDEHYDE				

made only 0.013 ppm. The CB4 mechanism predicted that the xylene side produced a PAN maximum of 0.11 ppm, only 25 percent more than observed (0.088 ppm) while predicting a PAN maximum of 0.047 for the toluene side, more than 3.5 times as much as observed (0.013 ppm) (see Figure 4). Formaldehyde predictions were in disagreement with observed measurement also. The measurements showed that in the toluene side, formaldehyde is produced a little sooner than in the xylene side, with a maximum of 0.077 ppm; the xylene side maximum is about 0.064 ppm. The CB4 mechanism predicted 0.26 ppm for the toluene side and 0.19 for the xylene side (see Figure 5). The CO predictions agree fairly well with the observed (but limited to before 1200 EDT) CO measurements. The xylene and toluene species are simulated very well (see Figure 6).

Equal carbon (3.0 ppmC) of m-xylene and o-xylene were compared for the same initial NO_x conditions on June 26, 1984. There appears to be differences in overall reactivity and some differences in NO_x chemistry. m-Xylene reacts faster than o-xylene. The PAN profile for m-xylene shows production initiated noticeably sooner than the o-xylene side: eventually producing more PAN. However the HCHO and CO profiles seem similar. The NO_x and O_3 results of June 26, 1984 are shown in Figure 7.

Quality Assurance and Facilities Description

An extensive (almost 300 pages) Quality Assurance and Facilites Description report has been prepared for this project.[2] It describes the facilities and instrumentation, calibration sources (including cross-comparisons and validation) and procedures, and includes a record of the calibrations performed during this period (including statistical analysis) for all the analytical methods and species. Normal operating procedures and methods for conducting experiments and transfer of data to insure error-free collection and transfer of data are described. The data processing procedures including computer programs and databases are explained. Examples of the format of the final documentation and data file are given. The Quality Assurance steps and checklists are given. The grading system used to generate the overall quality index for each experiment is explained.

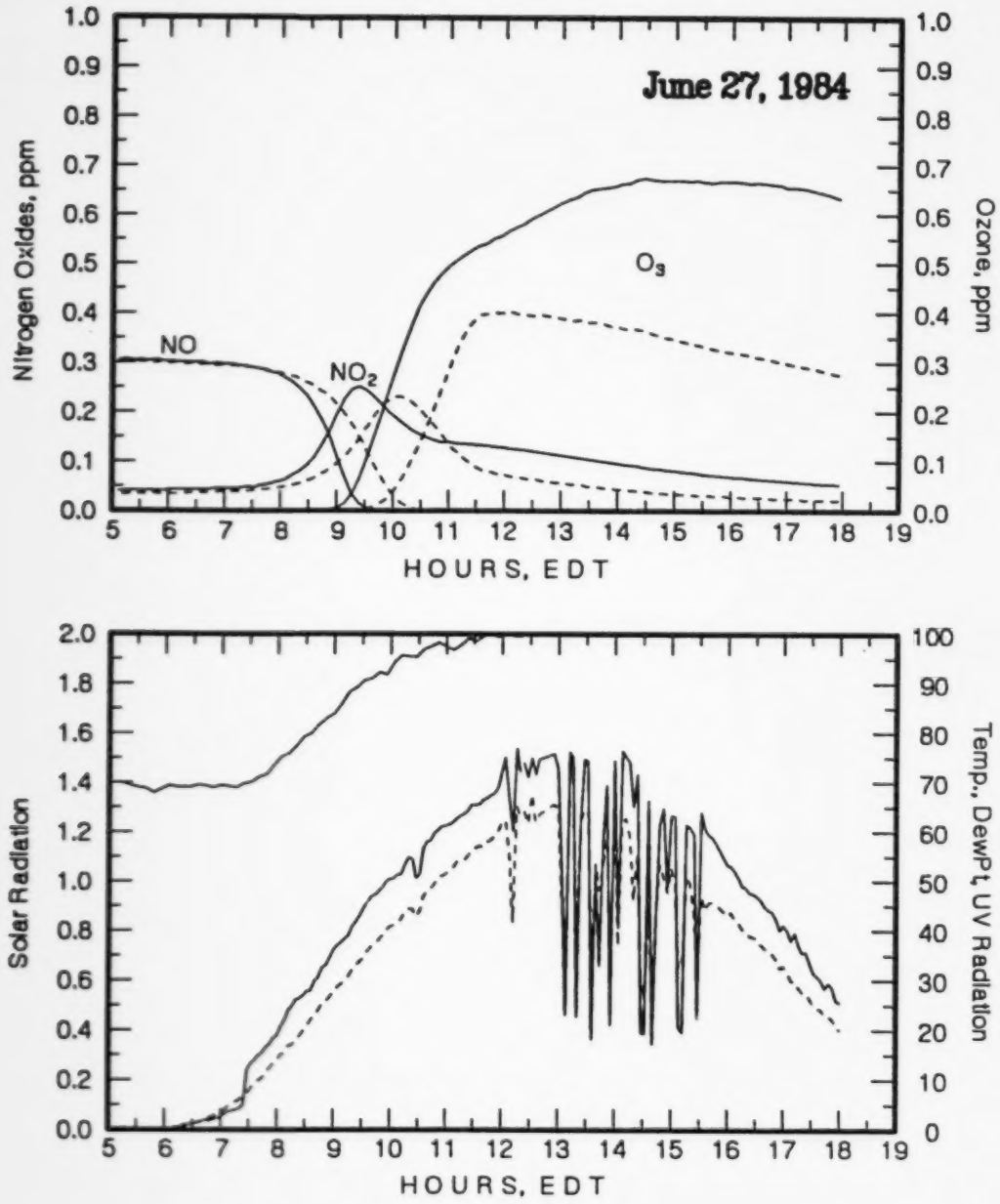

Figure 2. Toluene vs. m-Xylene
Top: (Solid) 2.0 ppmC m-Xylene;
(Dashed) 5.0 ppmC Toluene;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line, mcal-cm^{-2}-sec^{-1});

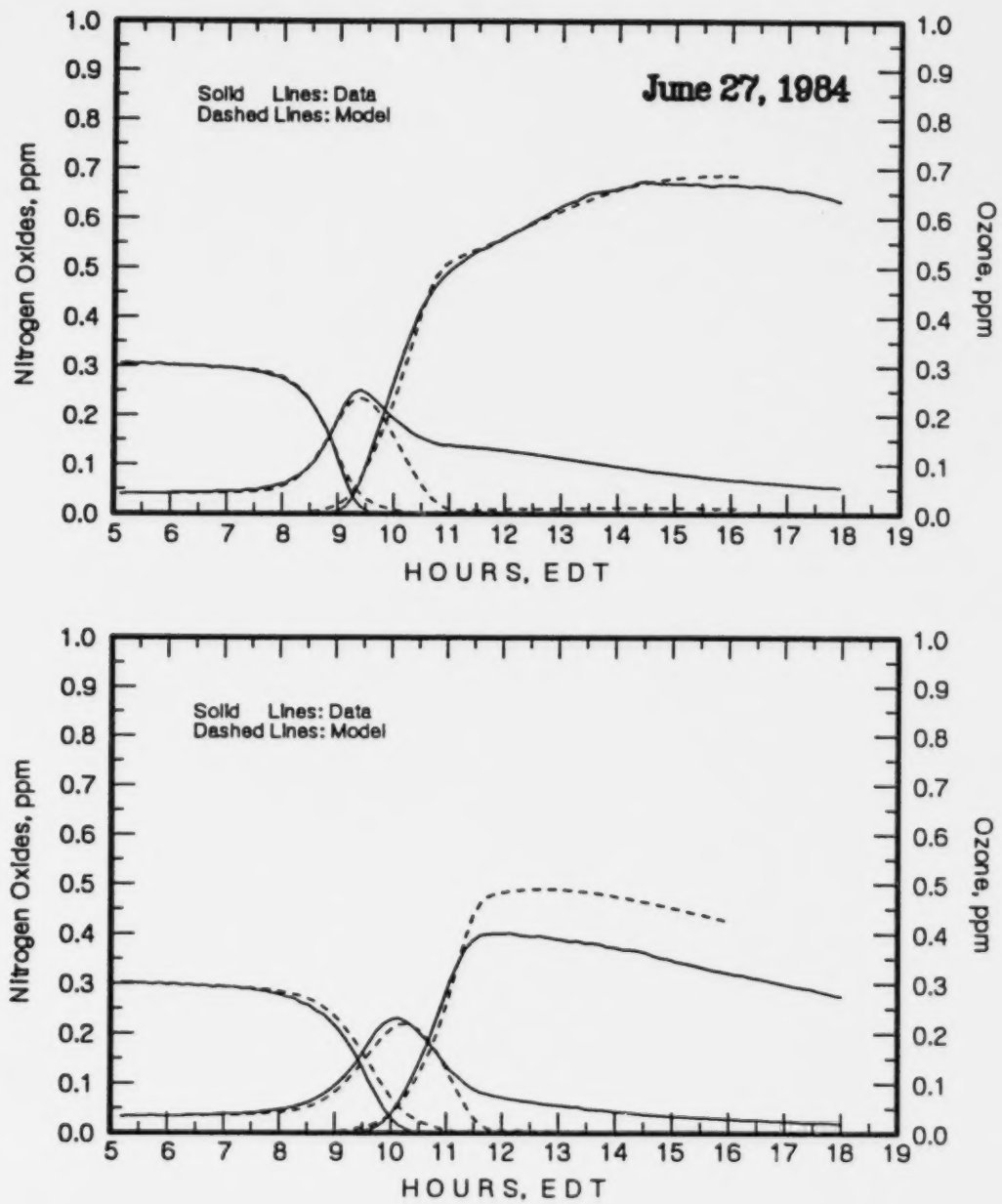

Figure 3. Toluene vs. m-Xylene
CB4: Standard Model Conditions;
NO_x and O_3 Simulation Results;
Top: 2.0 ppmC m-Xylene;
Bottom: 5.0 ppmC Toluene;

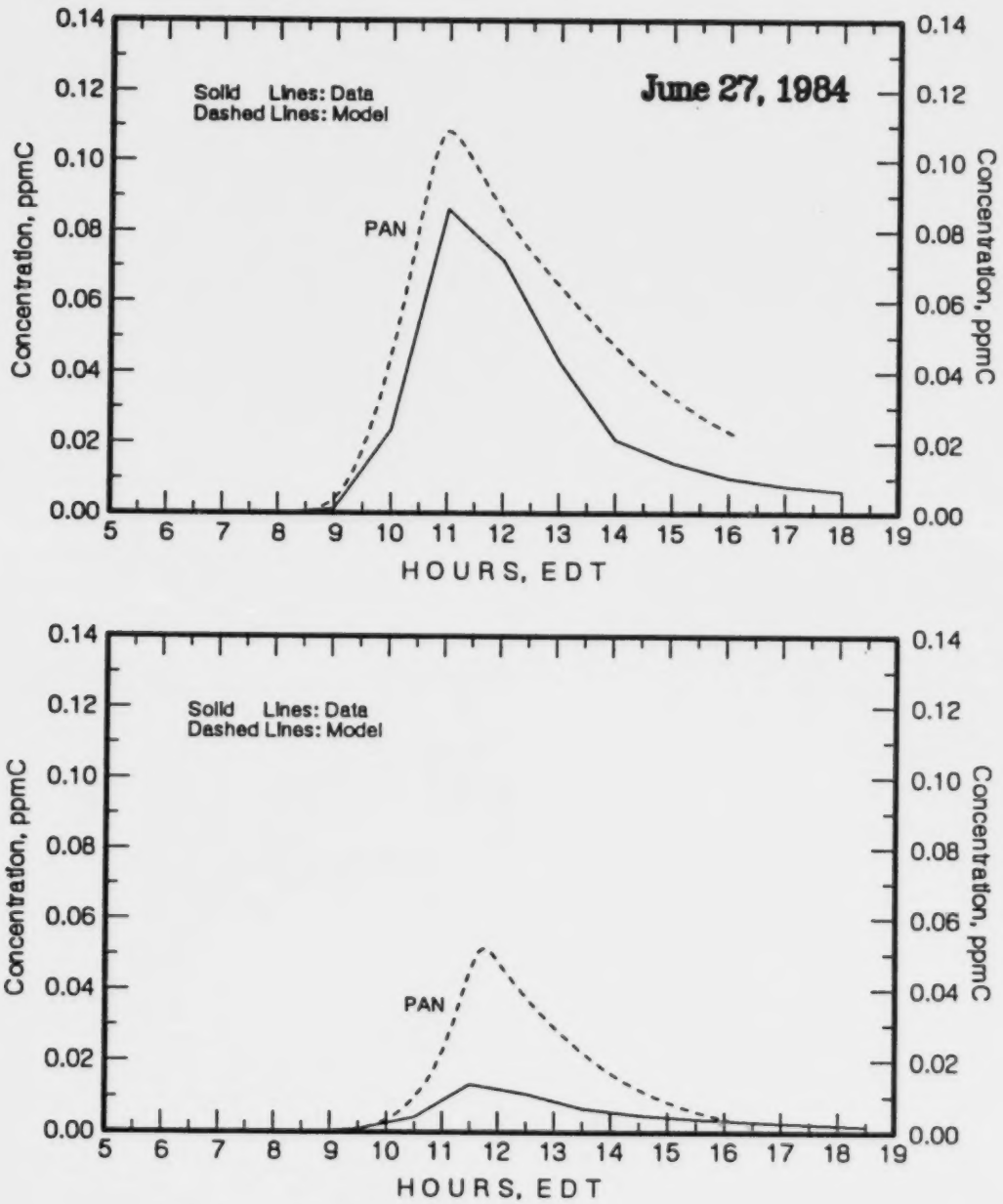

Figure 4. Toluene vs. m-Xylene
CB4: Standard Model Conditions;
PAN Simulation Results;
Top: 2.0 ppmC m-Xylene;
Bottom: 5.0 ppmC Toluene;

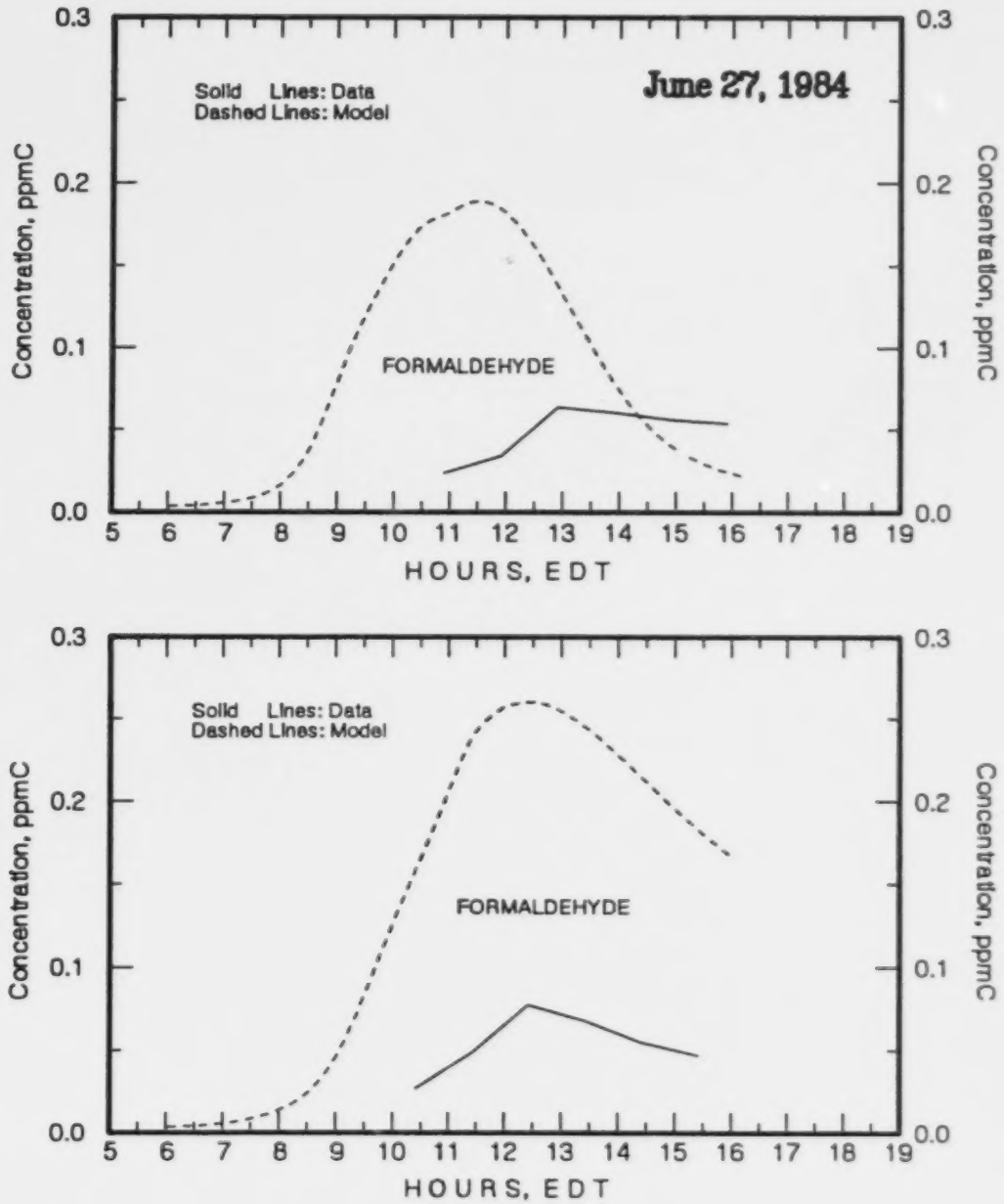

Figure 5. Toluene vs. m-Xylene
CB4: Standard Model Conditions;
HCHO Simulation Results;
Top: 2.0 ppmC m-Xylene;
Bottom: 5.0 ppmC Toluene;

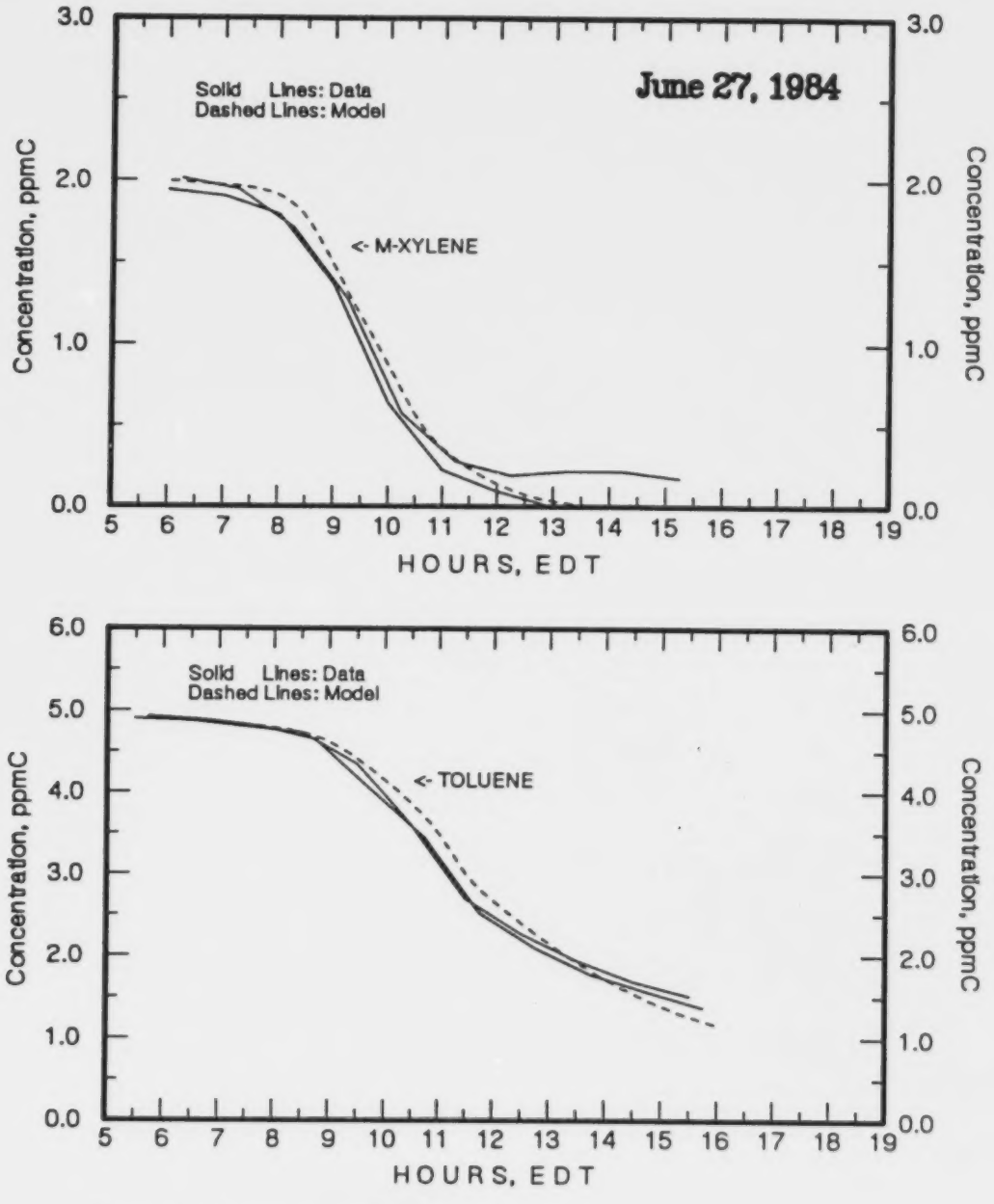

Figure 6. Toluene vs. m-Xylene
CB4: Standard Model Conditions;
m-Xylene and Toluene Simulation Results;
Top: 2.0 ppmC m-Xylene;
Bottom: 5.0 ppmC Toluene;

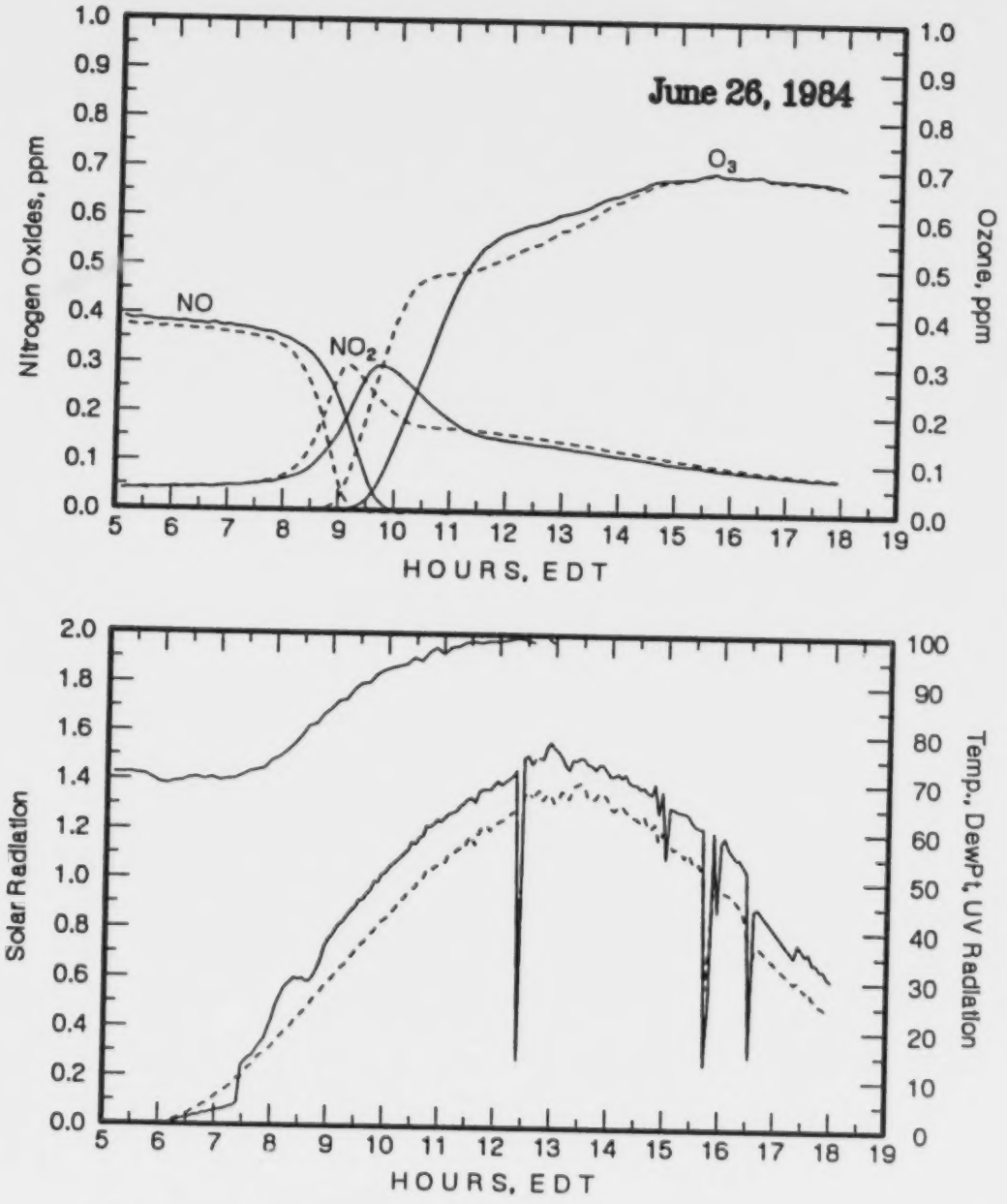

Figure 7. o-Xylene vs. m-Xylene
Top: (Solid) 3.0 ppmC o-Xylene;
(Dashed) 2.8 ppmC m-Xylene;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line, mcal-cm^{-2}-sec^{-1});

3

Model/Data Differences

Special experiments were conducted in order to resolve specific modeling problems. Several of these overlap with the other categories such as "Missing Experiments" since the problems are related to a lack of these experiments. In the introduction, the problems encountered in modeling a wide range of HC-to-NO_x ethylene runs were discussed. Additional experiments were conducted to resolve these problems. Since the runs were conducted with the assistance of the new and highly specific and sensitive tunable laser spectrophotometer system of Unisearch, these experiments are discussed in the later chaper (Assistance to Modelers) where the data obtained with the Unisearch analytical techniques are presented.

Mechanism developers started using two or more aromatic species in their mechanisms in an attempt to make the mechanisms capable of responding to variations in aromatic composition in the atmosphere. The experiments listed in Table 2 were to provide tests of the mechanisms ability to simulate variations in composition in the different types of aromatics and variation of HC-to-NO_xratio. The September 19 experiment is important since it is mostly the aromatic portion of the synthetic autoexhaust and urban mixtures (discussed later in this report).

Discussion Of Results From Example Experiments

An experiment conducted on August 29, 1985 varies the ratio of toluene to m-xylene between the two chamber sides while keeping the total carbon equal for both the total aromatics and total carbon by using equal amounts of the well studied, complex olefin/paraffin mixture UNCMIX. Each side contains 33 percent aromatics, 46 percent paraffins, and 21 percent olefins, which is a realistic distribution of basic HC classes in urban atmospheres. The BLUE side aromatic distribution is 75/25 m-xylene/toluene and the RED side is 25/75 m-xylene/toluene.

Table 2. Experiments Conducted To Resolve Problems

Date	CDI	HC	Ser	Proj	Q	I	P	Sun	Rank		
04-Sep-85	ONI	MC	08	ET	8	9	P	100	Satisfactory		
	Red Side			0.000	NOx			1.00	TOLUENE		
								0.50	ETHYLBENZENE		
								0.25	M-XYLENE		
								0.50	O-XYLENE		
								0.25	1,2,4-TMBENZENE		
								0.50	1,2,3-TMBENZENE		
	Blue Side			0.400	NOx			0.50	TOLUENE		
								0.50	ETHYLBENZENE		
								0.50	M-XYLENE		
								0.50	O-XYLENE		
								0.50	1,2,4-TMBENZENE		
								0.50	1,2,3-TMBENZENE		
29-Aug-85	ONI	MC	23	ET	7	9	P	88	Satisfactory		
	Red Side			0.400	NOx			2.00	UNCMIX		
								0.75	TOLUENE		
								0.25	M-XYLENE		
	Blue Side			0.400	NOx			2.00	UNCMIX		
								0.25	TOLUENE		
								0.75	M-XYLENE		
19-Sep-84	ONI	MC	33	ET	9	5	S	100	Best of kind		
	Red Side			0.339	NOx			4.38	HIMWAUTO		
	Blue Side			0.338	NOx			2.69	HIMWAUTO		

The modern mechanisms are designed to simulate this basic composition variation. These aromatics were chosen for this experiment since toluene is often represented explicity and m-xylene is often used as a surrogate for the remaining aromatics. Figure 8 shows the results. The BLUE side was approximately 40 minutes faster to crossover, 90 minutes faster to NO_2 maximum, and produced O_3 at least 30 minutes sooner. The BLUE side O_3 maximum was 1.02 ppm and the RED side was 0.77 ppm. Figure 9 shows HC time-concentration profiles of the aromatics which show the dramatic differences in reactivity between these compounds. The ethylene profiles show that the general mix used was well matched, and the more reactive side (more xylene) affected the reactivity of all the HCs.

Another important complex aromatic composition variation was conducted on September 4, 1985. This is a 6-component-aromatic-mixture comparison between equal NMHC concentration with variation of composition of three aromatics classes: two mono-, two di-, and two tri-methyl benzenes. It is designed to test new mechanistic representations of the differences in aromatic chemistries of different aromatic types. The results show some change in reactivity. Figure 10 shows the results for NO_x and O_3. Figure 11 shows the profiles of most of the HCs used in the experiment. Notice the large differences in reactivity.

Another important experiment conducted September 19, 1984 are two HC-to-NO_x ratio systems with the mostly aromatic, high molecular weight portion (HiMW) of the synthetic autoexhaust and synthetic urban mixture (4.4 vs 2.7 ppmC – matched NO_x = 0.32 ppm). This experiment gives modelers a chance to model the important fraction of autoexhaust which seems to provide the most difficulty for the chemical mechanisms. Successfully modeling of these two sides without changing chamber assumptions is a prerequisite to successfully modeling the series of low and high HC-to-NO_x ratio synthetic autoexhaust and synthetic urban experiments. Figure 12 shows the results for NO_x and O_3.

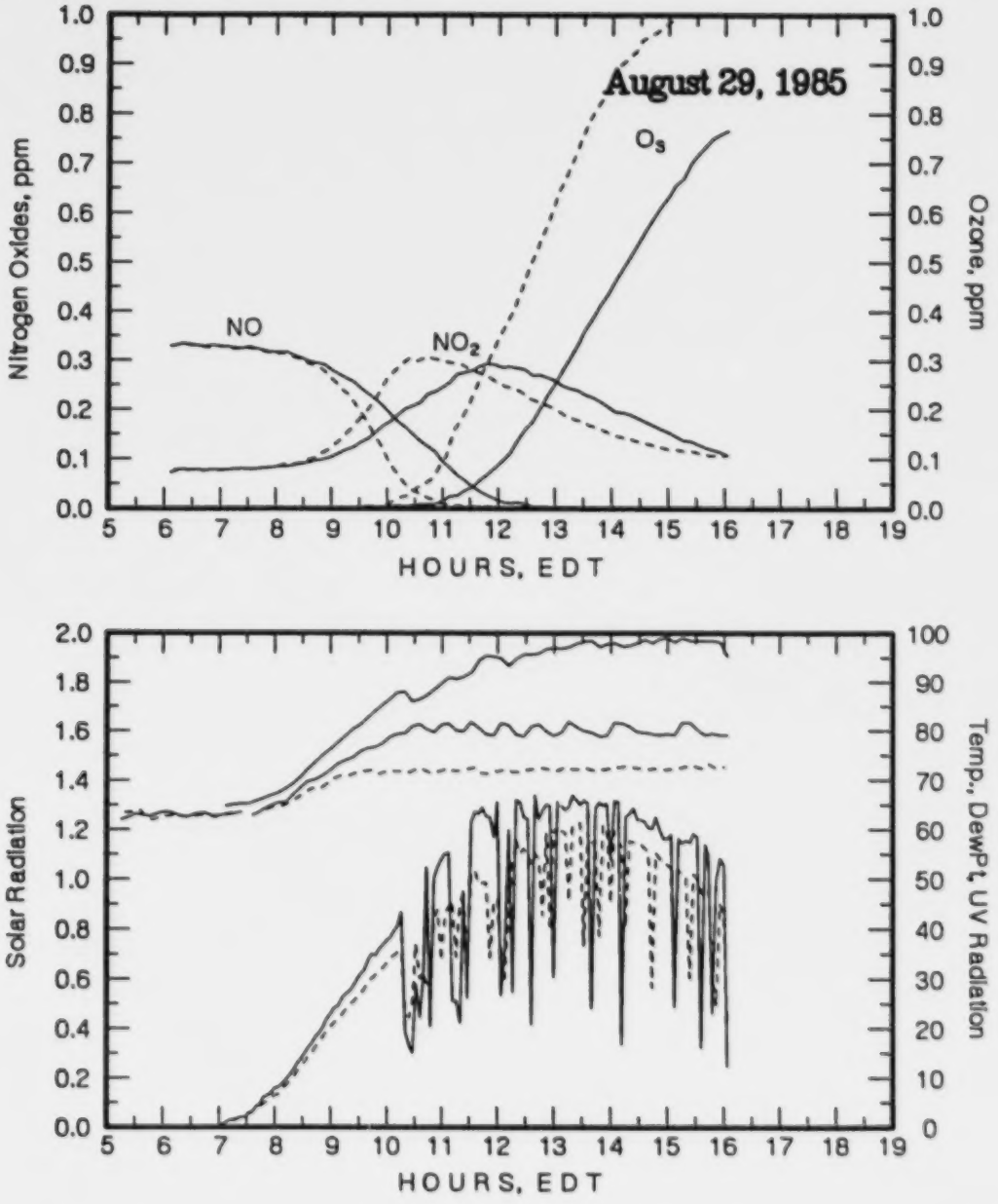

Figure 8. 1 ppmC 25/75 vs 1 ppmC 75/25 Toluene / m-Xylene; 2 ppmC UNCMIX both;
Top: (Solid) 0.75 ppmC Toluene, 0.25 ppmC m-Xylene and 2.0 ppmC UNCMIX;
(Dashed) 0.25 ppmC Toluene , 0.75 ppmC m-Xylene and 2.0 ppmC UNCMIX;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line, mcal-cm^{-2}-sec^{-1});

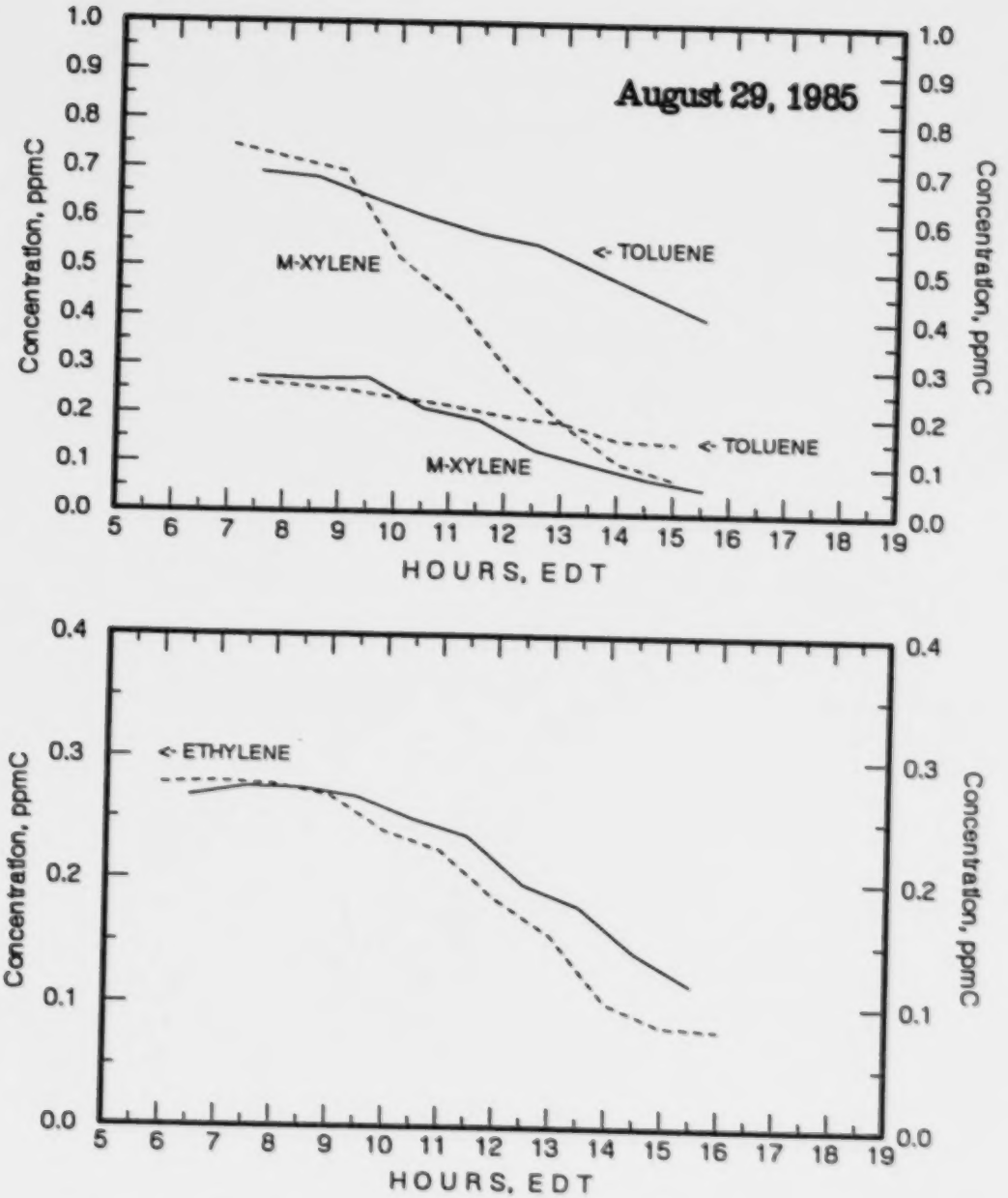

Figure 9. 1 ppmC 25/75 vs 1 ppmC 75/25 Toluene / m-Xylene; 2 ppmC UNCMIX both; Selected Hydrocarbon Data.

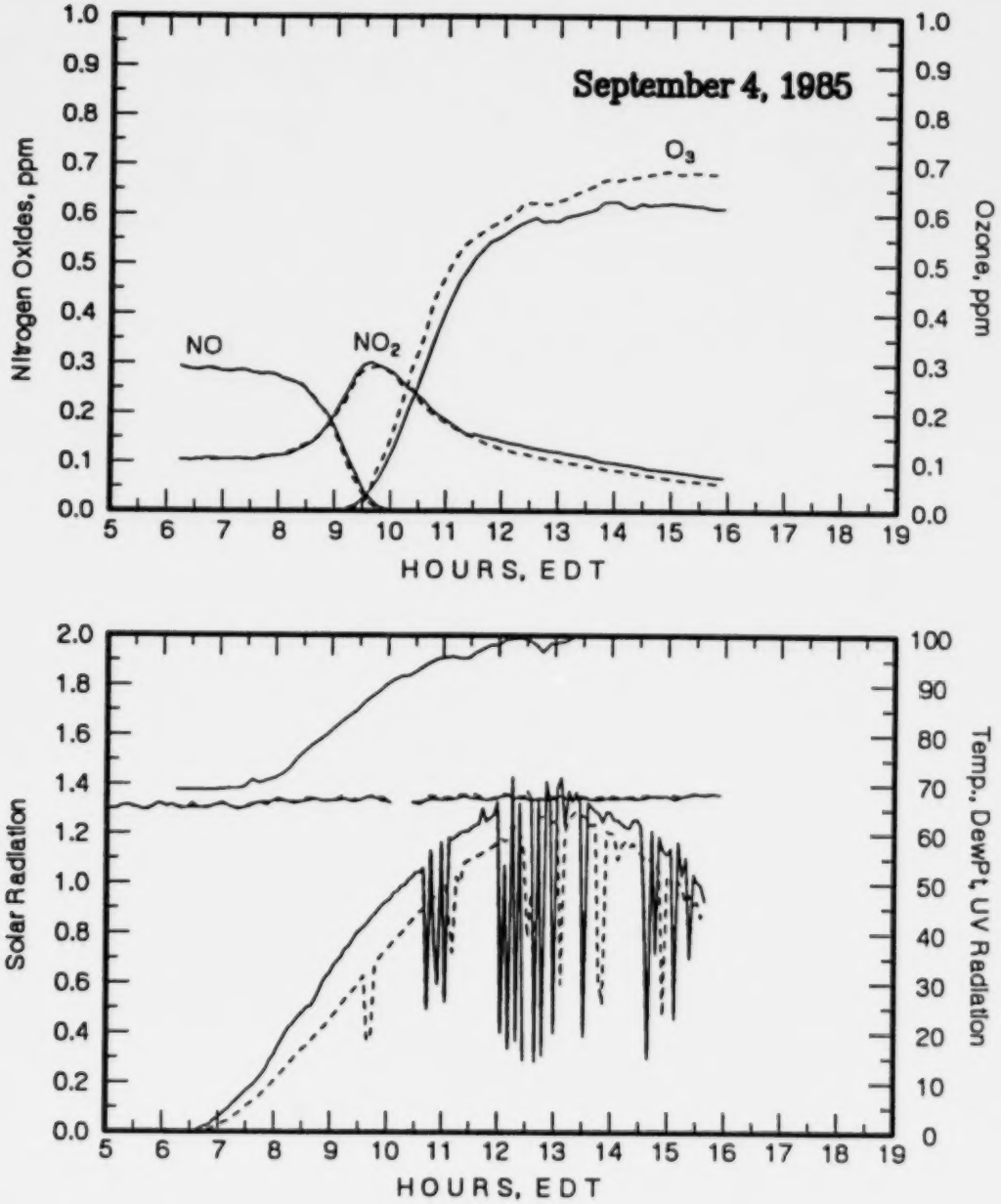

Figure 10. Complex Aromatic Composition Variation.
Top: (Solid) 3.1 ppmC total; High Toluene fraction;
(Dashed) 3.06 ppmC total ; Low Toluene fraction;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line, mcal-cm^{-2}-sec^{-1});

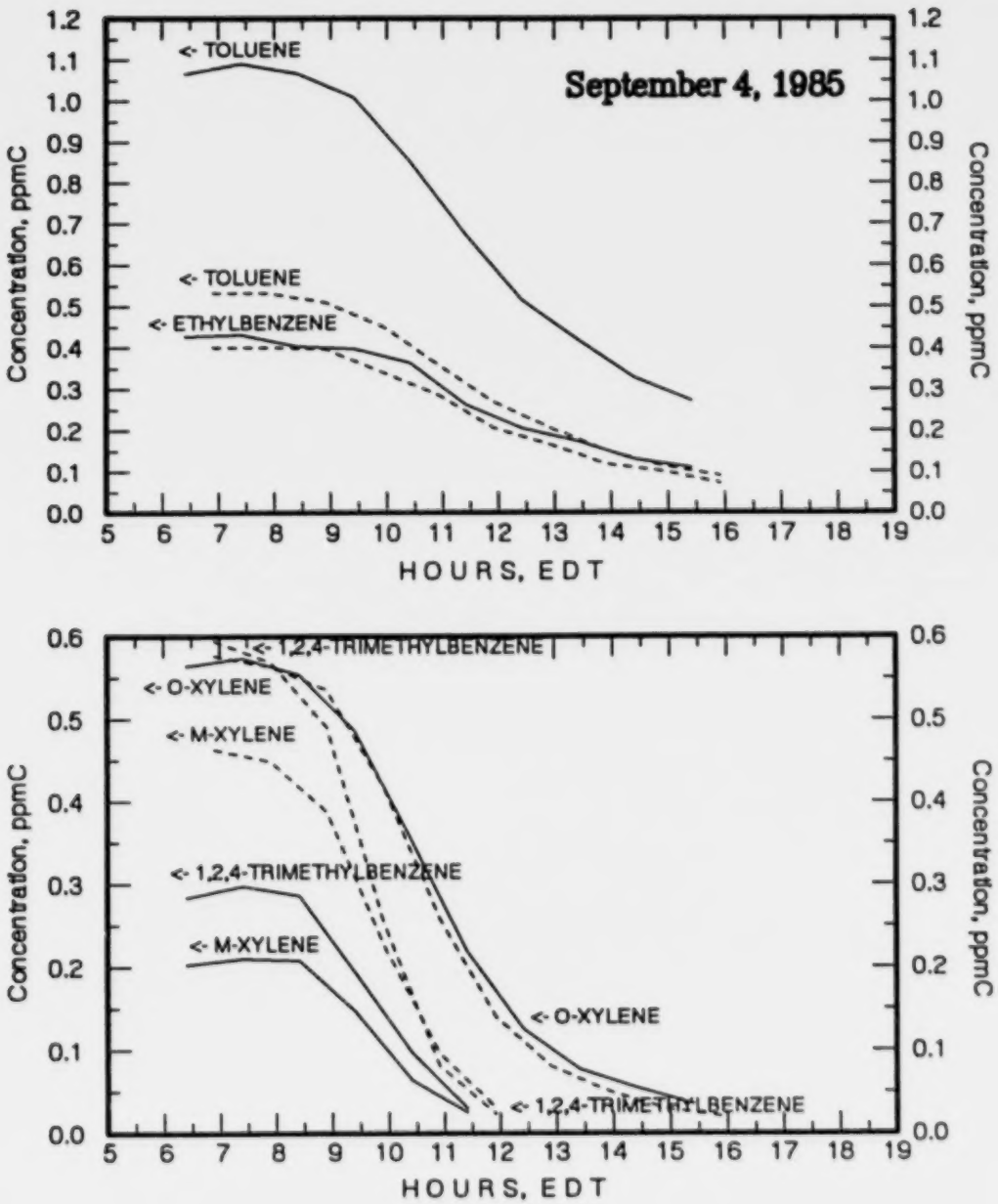

Figure 11. Complex Aromatic Composition Variation.
Selected Hydrocarbon Data.

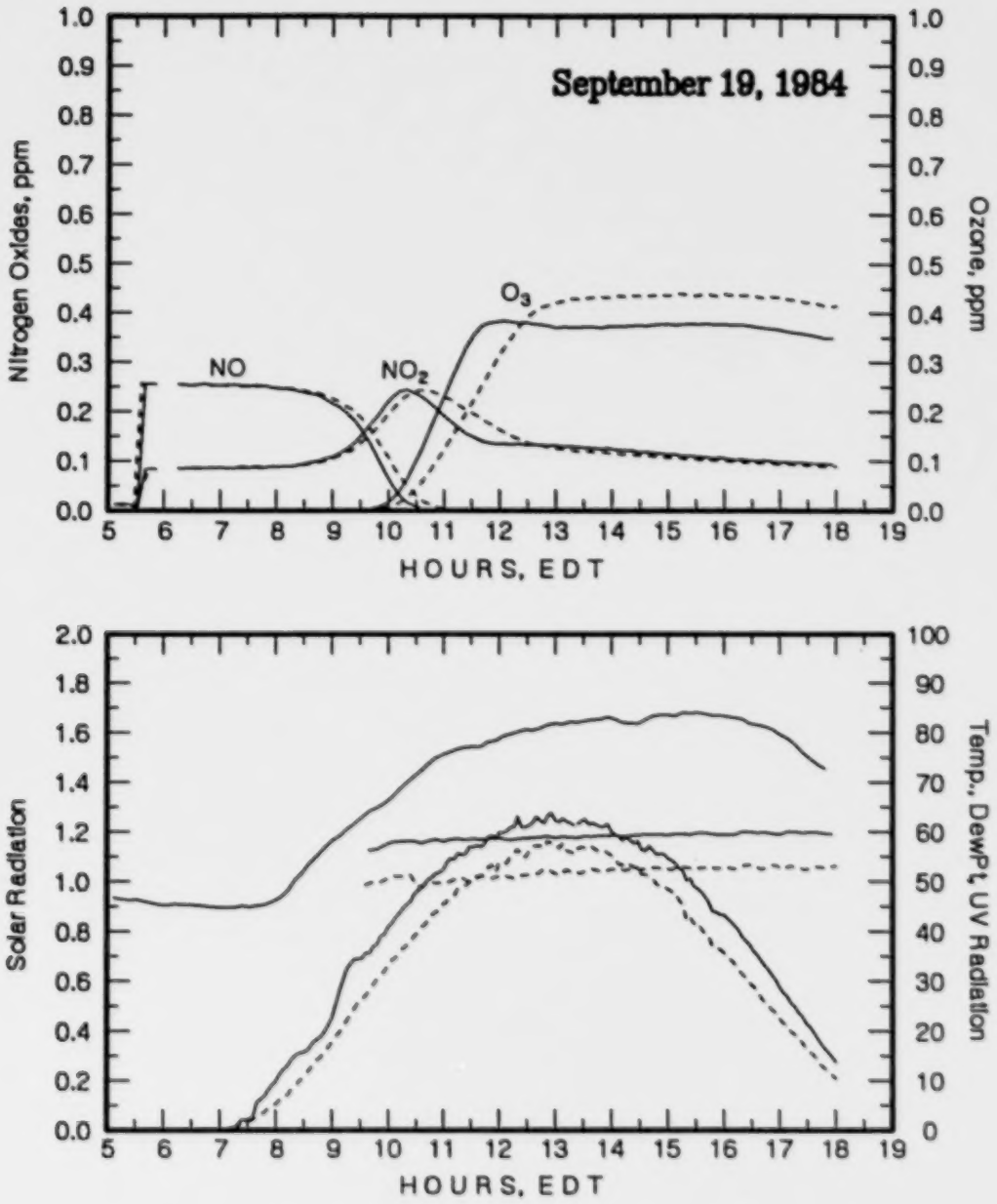

Figure 12. 4.4 ppmC vs. 2.7 ppmC Complex Aromatic HC-to-NO_x Variation;
Top: (Solid) 4.4 ppmC Mostly Aromatic Mixture;
(Dashed) 2.7 ppmC Mostly Aromatic Mixture;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line, mcal-cm^{-2}-sec^{-1});

4

Urban-Like Conditions

Photochemical models are used to predict ozone for current and post-control initial conditions of various compositions. Several important types of experiments were conducted in this set to extend the range of urban conditions to more completely test this important function. The dual-nature of the UNC Outdoor smog chamber allows for two sets of conditions to be irradiated with the same solar light and natural temperature variation. Several examples will be shown.

Most of the experiments conducted during this study utilized the more urban-like hydrocarbon mixtures. About 20 percent were of the "Delta Hydrocarbon" series, to provide a test of the mechanisms ability to simulate the effect of hydrocarbon control. About 25 percent of the experiments were substitution of various hydrocarbons (suggested by the EPA) or other aromatics, into synthetic urban-mix and automobile exhaust, for testing of chemical mechanisms. About 5 percent were designed to test the importance of the small formaldehyde fraction included in the urban-like mixes. The remaining experiments were for characterization and demonstration of the ability to match the chemical conditions in the chamber sides.

Design of Synthetic HC Mixtures

SynAuto

One of the tasks in the UNC automobile exhaust project was to test the hypothesis that a synthetic mixture of 10–15 compounds could adequately represent the reactivity of dilute automobile exhaust. From the concentration and identity of the compounds in the exhaust, we prepared a 13-component mixture that would mimic the overall reactivity of the exhaust. The mixture, listed in Table 3, contained 3 paraffins, 4 olefins, 5 aromatics, and formaldehyde. Details on the types

Table 3. Composition of Hydrocarbon Mixtures.
(Units are fraction of total carbon)

Compound	UNCMIX	SynAuto	SynUrban
butane		0.0391	0.1000
pentane	0.2531		0.1367
isopentane	0.1484	0.0519	0.0801
2-methylpentane	0.0996		0.0538
2,4-dimethylpentane	0.0864		0.0467
2,2,4-trimethylpentane	0.1202	0.1121	0.1340
ethylene	0.1167	0.2391	0.0630
propylene	0.0524	0.0416	0.0238
1-butene	0.0254	0.0196	0.0137
trans-2-butene		0.0196	
cis-2-butene	0.0313		0.0169
2-methyl-1-butene	0.0347		0.0187
2-methyl-2-butene	0.0317		0.0171
benzene		0.0538	0.0331
toluene		0.2115	0.1304
m-xylene		0.1026	0.0633
o-xylene		0.0481	0.0296
1,2,4-trimethylbenzene		0.0564	0.0347
formaldehyde		0.0200	0.0200
total paraffin	0.7077	0.2031	0.5404
total olefin	0.2922	0.3199	0.1546
total aromatic	0.0000	0.4724	0.2854

of vehicles, comparisons with a large test fleet, and other experimental results are provided elsewhere.[3]

In the project, four dual experiments were performed in which exhaust from one of the vehicles was injected into one side of the chamber and an "equivalent" amount of synthetic exhaust was injected into the other side. One example of a well-matched system was October 4, 1983. In this experiment, 2.6 ppmC of exhaust from a 1972 V8 Dodge Charger and 2.2 ppmC of the synthetic mix (less because acetylene which is of low reactivity, constituted ≈15% of the exhaust) showed a remarkably similar reactivity (time to NO-to-NO_2 crossover agreed to within 8 minutes and O_3 maxima agreed to within ≈6%). Thus we believe that the synthetic mixture called SynAuto in Table 3 is a reasonable approximation of automobile exhaust reactivity.

SynUrban

A second mixture, more typical of urban-like conditions, was also used in this study. Both emissions inventory and atmospheric hydrocarbon data were the basis for the compositional design of this synthetic urban mixture (SynUrban).

In 1972 Kopczynski investigated ambient HC compositions in both Los Angeles and Cincinnati.[4] Kopczynski used these data to design a mix for smog chamber use. His mix was used by UNC in 1973 as a guide to preparing a synthetic urban mixture, called UNCMIX which is also listed in Table 3. UNCMIX is made from two different mixtures: a paraffins and olefins mix, which is stored in a pressurized tank, and an aromatics mix, which because of its significantly lower vapor pressure, is stored as a liquid mixture. UNCMIX has been used in more than 100 experiments in our chambers; most of these experiments, however, have used only the paraffin and olefin portion of the mixture.

In conducting this study, we wished to use newer ambient data for the mixture design. Killus and Whitten[5] conducted a review of ambient data to provide the basis for their recommended default composition for air quality modeling in cases of insufficient support data. They found that NMHC composition did not vary greatly between cities. Gipson[6] recently completed an analysis of atmospheric data collected for the Northeast Corridor Regional Modeling Project. He also found little variation among the 435 sites in both the composition and the average carbon number of each HC class fraction.

It was decided to design a synthetic urban mixture which would come close to matching the default composition of Killus and Whitten, once converted to Carbon Bond Units. These values are listed in Table 4.

Table 4. Default Carbon Bond Class Fractions as Recommended by Killus and Whitten for CB3[5]

Bond Group	Meaning	Range	Default
PAR	all single bonded carbon	0.50 – 0.70	0.58
ETH	ethylene carbon	0.02 – 0.11	0.04
OLE	all double bonded carbon	0.02 – 0.07	0.03
ARO	all aromatic ring carbon	0.10 – 0.40	0.19
CARB	carbonyl group carbon	0.03 – 0.10	0.05
NR	non-reactive carbon	0.05 – 0.20	0.15

Although these indicate the total class fractions, they do not give the class average carbon numbers and therefore these do not suggest the types of species that should be included in the mixture.

Average carbon numbers, as determined by the Gipson analysis[6] , were used to estimate the species needed in each class (see Table 5).

Table 5. Average Carbon Number at Northeast Corridor Regional Modeling Sites

	Paraffin	Olefin	Aromatic
mean	5.4	2.9	7.7
sd	0.4	0.7	0.02

The average composition for all 435 sampling sites was also used as a guide to designing the synthetic hydrocarbon mixture (see Table 6).

Table 6. Average Composition at
Northeast Corridor Regional Modeling Sites
(analysis of ambient HC data)

Class	mean %C	s.d.
Paraffin	56.4	9.5
Olefin	10.5	4.9
Aromatic	27.1	8.2
Acetylene	2.7	1.6
Ethane	3.3	2.5

The composition of the designed SynUrban mixture is given in Table 3. It consisted of 18 compounds: 6 paraffins, 6 olefins, 5 aromatics, and formaldehyde. Its composition in terms of the Carbon Bond Mechanism input species is given in Table 7; these can be compared with the default values listed in Table 4.

Table 7. Carbon Bond 3 Class Fraction for SynUrban Mixture.
(units are fraction of total carbon)

Class	Carbon %
PAR	0.5498
ETH	0.0533
OLE	0.0281
ARO	0.1710
CARB	0.0299
NR	0.1680

Delta Hydrocarbon Initial Conditions

Shown first are basic Delta HC experiments with the synthetic urban-like mixtures without any additional substitution, such as conducted on August 5 and 6, 1984 (low and mid HC-to-NO_x ratio synthetic automobile exhaust) and September 2, 1984 and June 26, 1985 (low and mid HC-to-NO_x ratio synthetic urban mixture). In each day's experiment the initial NO_x concentrations are matched in each chamber side and the composition of the HC is the same: one side has about 33 percent less HC. For the higher–HC-to-NO_x ratio (9.3:1) August 6 experiment conducted with the SynAuto mixture, HC control results in only a 6 percent reduction in O_3 maximum, although production is delayed by about one hour. This system is NO_x limited. That is, both systems (sides) had sufficient HC to oxidize all the NO_x. In a NO_x limited system (constant HC composition), the maximum O_3 is essentially determined by the availability of NO_x and not the HC in the system. Picture an O_3 isopleth diagram with the initial conditions location as being on the right and below the O_3 maximum ridge line. In this area, O_3 maximum concentrations are not very dependent upon HC. The time to reach O_3 maximum, however, is dependent upon the reactivity and concentration of the HC. For the lower HC-to-NO_x ratio (3.7:1) August 5 experiment, 31 percent less HC (SynAuto mixture) resulted in a 43 percent reduction in O_3 maximum. For these lower HC-to-NO_x conditions, HC control has much more effect. The results of August 5 and 6, 1984 are shown in Figure 13.

As would be expected, at the same total HC, the SynUrban mix is less reactive than the SynAuto mix because the SynUrban mix design takes into account all urban sources, many of which are much less reactive than automobile exhaust. There is a much larger $\Delta O_3/\Delta HC$ for the SynUrban mix than for the SynAuto mix, another reflection of its lower overall reactivity. The September 2 experiment shows that the 1 ppmC system (HC-to-NO_x ratio = 3.5:1) is very sensitive to HC concentration, in that 1.1 ppmC of SynUrban made about 0.12 ppm O_3 and 0.8 ppmC of SynUrban made only 0.02 ppm O_3: a reduction of 83 percent for a hydrocarbon control of 31 percent. A higher HC-to-NO_x ratio (13.6:1) experiment was conducted on June 26, where a 39 percent control of HC resulted in a 20 percent reduction in the O_3 maximum concentration. The results of September 2, 1984 and June 26, 1985 are shown in Figure 14.

Table 8 lists the Delta–type experiments conducted, separated by series.

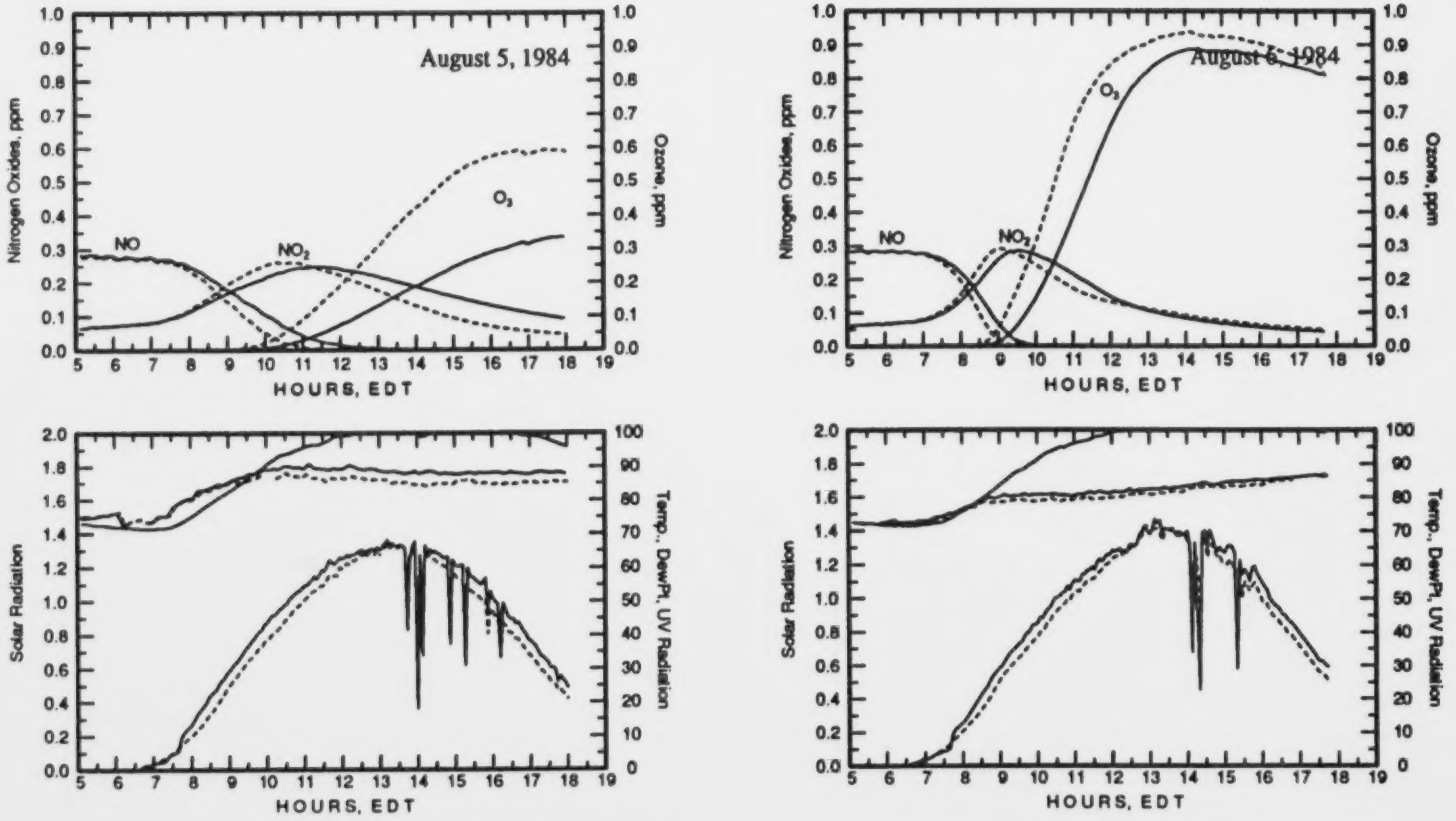

Figure 13. Low and Mid HC-to-NO_x SYNAUTO:
Left: 1.3 vs. 0.9 ppmC SYNAUTO; Right 3.3 vs. 2.3 ppmC SYNAUTO;
Bottom: RED chamber air temperature (top solid line, °F); RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radiation (solid line, cal-cm^{-2}-sec^{-1}); ambient ultraviolet radiation (dashed line, mcal-cm^{-2}-sec^{-1});

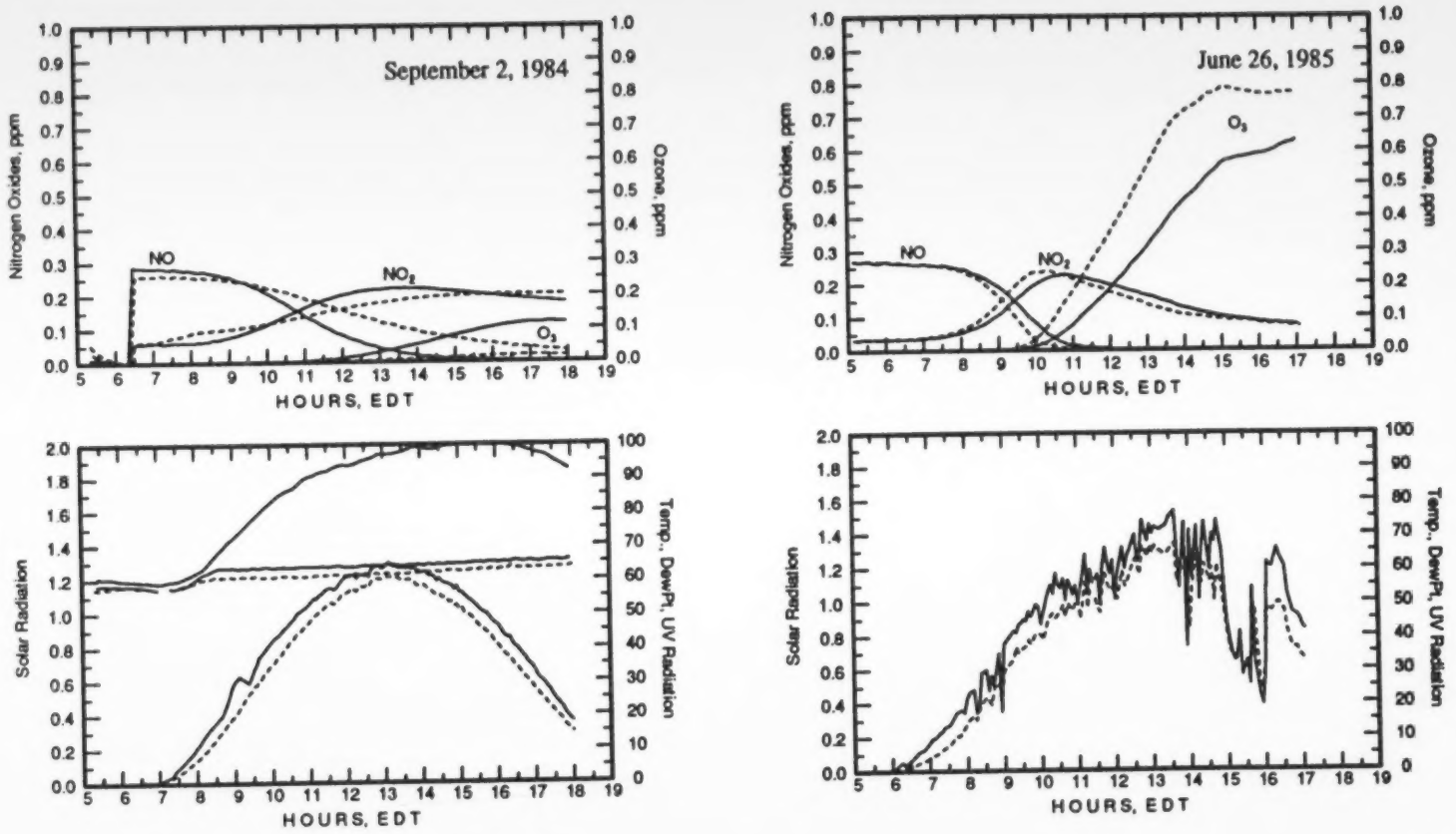

Figure 14. Low and Mid HC-to-NO_x SYNURBAN:
Left: 1.2 vs. 0.8 ppmC SYNURBAN; Right 3.1 vs. 2.3 ppmC SYNURBAN;
Bottom: RED chamber air temperature (top solid line, °F); RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radiation (solid line, cal-cm^{-2}-sec^{-1}); ambient ultraviolet radiation (dashed line, mcal-cm^{-2}-sec^{-1});

Table 8. Delta–HC, Urban Conditions Experiments

```
>>>>> For the Series type of 34 DELTA NOx <<<<<

-------------------------------------------------
  Date  CDI HC Ser  Proj Q I P  Sun  Rank
-------------------------------------------------

18-Oct-84 ONI MC 34   ET 6 7 P  0  Best of kind

      Red Side  0.300 NOx   3.00   SYNAUTO84
      Blue Side 0.200 NOx   3.00   SYNAUTO84

Number of runs of this series is 1

>>>>> For the Series type of 33 DELTA HC <<<<<

05-Aug-84 ONI MC 33   ME 9 6 S  92  Best of kind

      Red Side  0.351 NOx   0.93   SYNAUTO84
      Blue Side 0.345 NOx   1.33   SYNAUTO84

06-Aug-84 ONI MC 33   ME 9 5 S  86  Best of kind

      Red Side  0.351 NOx   2.29   SYNAUTO84
      Blue Side 0.355 NOx   3.29   SYNAUTO84

02-Sep-84 ONI MC 33   ME 9 5 S  100  Satisfactory

      Red Side  0.344 NOx   1.24   SYNURBAN
      Blue Side 0.322 NOx   0.82   SYNURBAN

08-Sep-84 ONI MC 33   ME 8 4 S  86  Satisfactory

      Red Side  0.352 NOx   1.92   SYNAUTURB
      Blue Side 0.321 NOx   2.84   SYNAUTURB
```

Table 8. cont. Urban Conditions Experiments

Date	CDI	HC	Ser	Proj	Q	I	P	Sun	Rank
25-Jun-85	ONI	MC	33	ME	6	9	S	85	Satisfactory
	Red Side	0.350	NOx	2.00	SYNURBAN				
	Blue Side	0.350	NOx	3.00	SYNURBAN				
26-Jun-85	ONI	MC	33	ME	9	9	S	94	Best of kind
	Red Side	0.299	NOx	2.27	SYNURBAN				
	Blue Side	0.300	NOx	3.10	SYNURBAN				

Formaldehyde Effects On HC Reactivity

Another set of important experiments studied the effect of a small formaldehyde fraction in complex mixtures. Figure 15 shows the results of the experiment conducted on September 21, 1984. Matched injections (2.4 ppmC) of a variation of the synthetic autoexhaust (the normal 2 % formaldehyde not included as well) were made into the two chamber sides. Formaldehyde (0.18 ppm, 7.5 percent of NMHC) was added to one side. The side with the HCHO was 40 minutes faster to NO-to-NO_2 crossover and one hour sooner to O_3 maximum, producing an 8 percent greater O_3 maximum. The HC-to-NO_x ratio of this experiment was 6.7. Figure 16 also shows the effect of formaldehyde composition variation within the total initial NMHC. Two chamber sides were compared where UNCMIX was substituted with 5 vs 10 percent of HCHO in a 3 ppmC matched NMHC /NO_x system (October 1, 1985). The initial NO_x was much lower than usual resulting in a HC-to-NO_x ratio of 17.5. Because the higher HC-to-NO_x ratio experiments are already reactive, the variation of the HCHO fraction within the initial NMHC conditions had less dramatic effect between the two sides. These two experiments conducted on September 21, 1984 and October 1, 1985 will provide modelers with a wide range of conditions for model testing.

Table 9 lists the experiments conducted to test the importance of aldehydes.

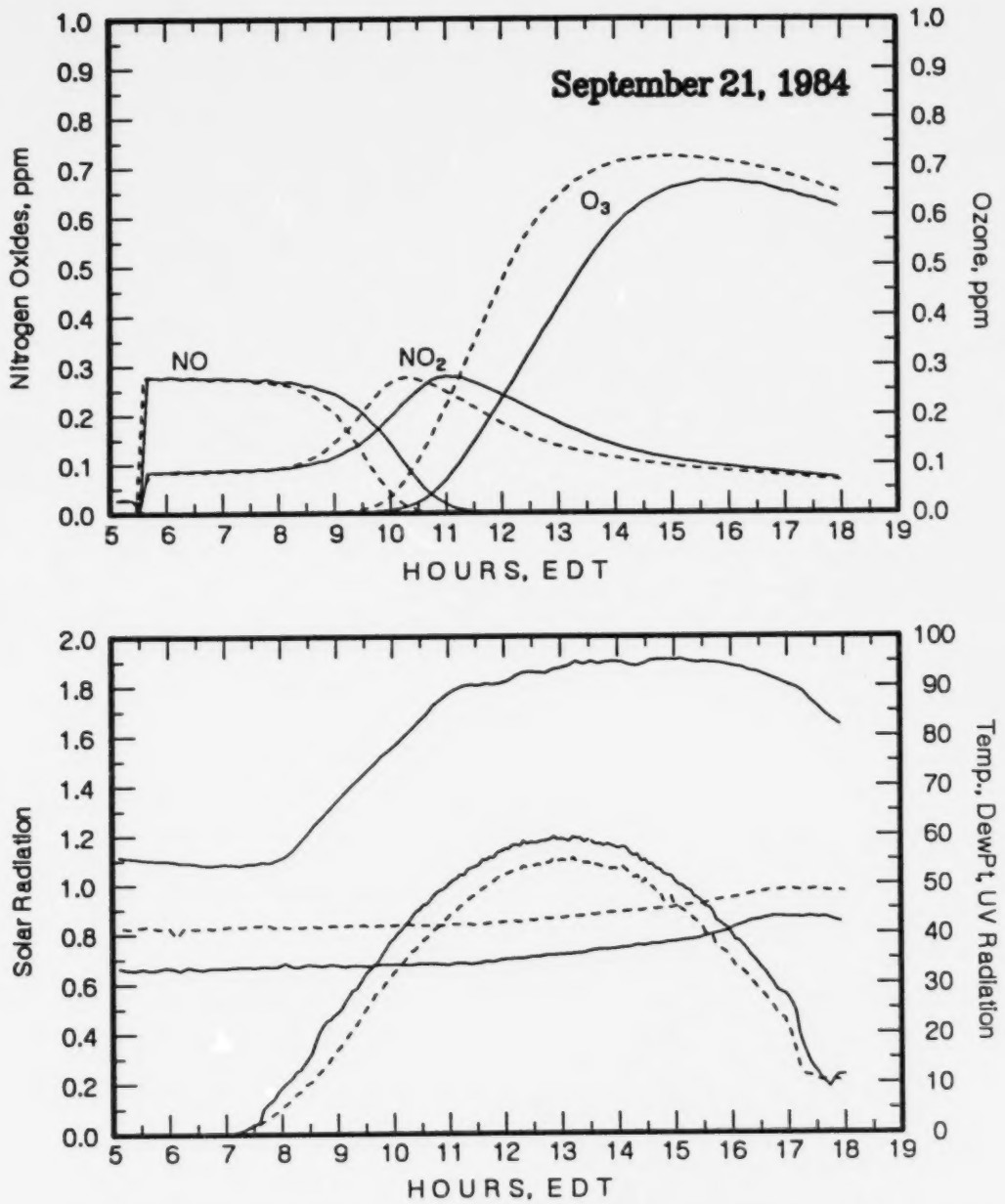

Figure 15. Matched 2.4 ppmC SYNAUTURB; 0.18 ppmC HCHO added to one side.
Top: (Solid) 2.4 ppmC SYNAUTURB;
(Dashed) 2.4 ppmC SYNAUTURB plus 0.18 ppmC HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line, mcal-cm^{-2}-sec^{-1});

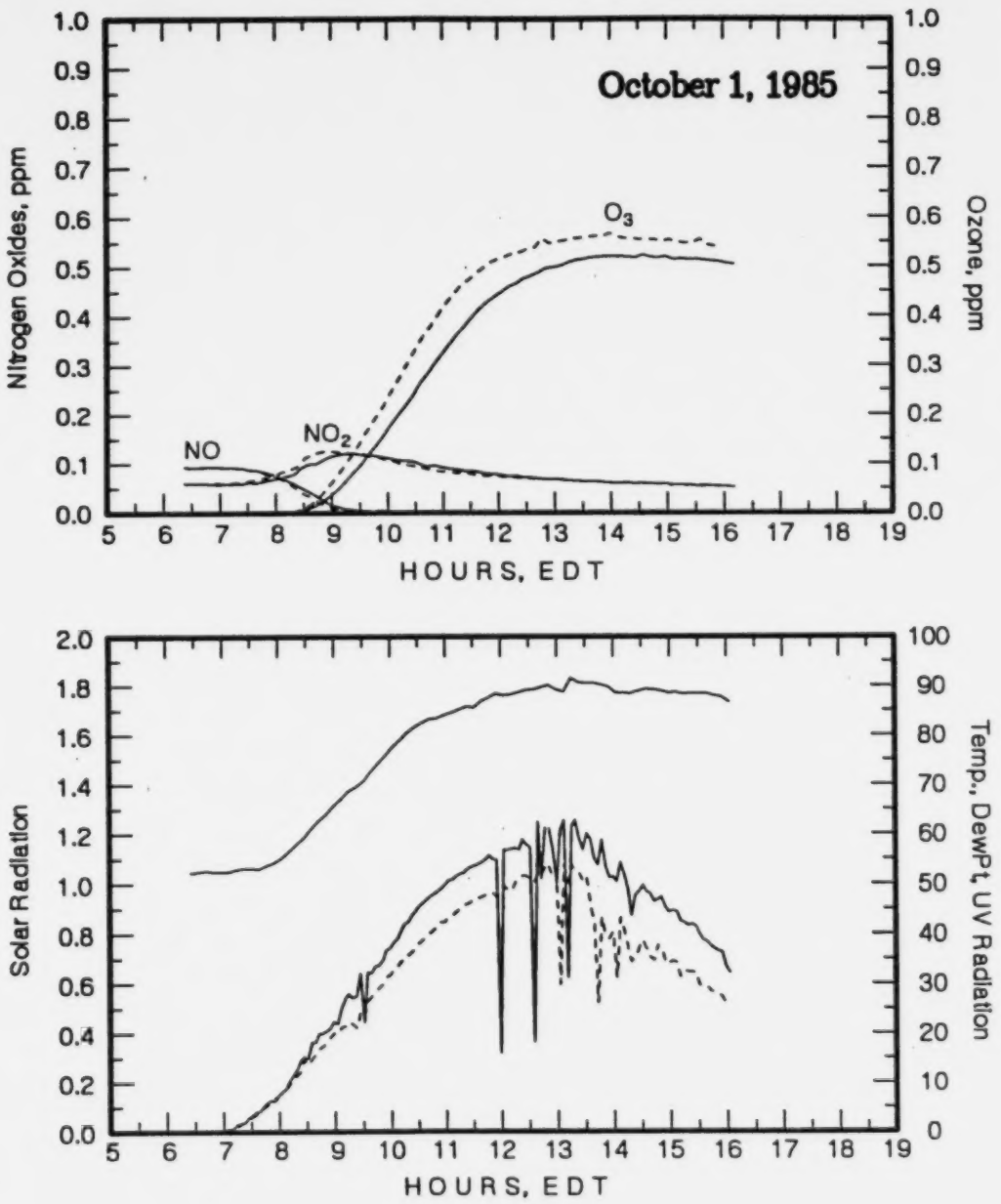

Figure 16. Effect of Formaldehyde (5 vs.10 %) Substituted in UNCMIX;
Top: (Solid) 2.85 ppmC UNCMIX plus 0.15 ppmC HCHO;
(Dashed) 2.7 ppmC UNCMIX plus 0.3 ppmC HCHO;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line, mcal-cm^{-2}-sec^{-1});

Table 9. Aldehyde/Urban-Mix Experiments

Date	CDI	HC	Ser	Proj	Q	I	P	Sun	Rank
>>>>> For the Series type of 29 Addition, Aldehyde <<<<<									
21-Sep-84	ONI	MC	29	ET	9	5	S	100	Satisfactory
Red Side	0.363	NOx	2.40	SYNTHETIC AUTO EXHAUST					
Blue Side	0.359	NOx	2.39	SYNTHETIC AUTO EXHAUST					
			0.18	FORMALDEHYDE					
01-Oct-85	ONI	MC	33	ET	8	9	P	97	Satisfactory
Red Side	0.080	NOx	2.85	UNCMIX					
			0.15	FORMALDEHYDE					
Blue Side	0.080	NOx	2.70	UNCMIX					
			0.30	FORMALDEHYDE					
17-Oct-85	TNI	MB	33	ET	8	9	P	78	Satisfactory
Red Side	0.500	NOx	2.00	SIMMIX2					
			0.10	FORMALDEHYDE					
Blue Side	0.500	NOx	2.00	SIMMIX2					
			0.05	FORMALDEHYDE					

5

Assistance For Modelers

Many experiments were conducted as requested by different modelers. Experiments with principal single compounds such as ethylene and propylene and NO_x were performed to monitor the formation of formaldehyde, nitric acid, and hydrogen peroxide using new highly sensitive analytical techniques. Hydrogen peroxide experiments (using large initial concentrations) were conducted. Other experiments were conducted as suggested by different scientists utilizing various compounds such as N_2O to study the photolysis of O_3, and butane and biacetyl for characterizing the chamber. These experiments are listed in Table 10 by series. The results of various examples of the different types of experiments are discussed in following sections.

Special Techniques For HCHO, H_2O_2, HNO_3, NO_2

The Unisearch Tunable Laser system for formaldehyde, hydrogen peroxide, nitric acid, and the Luminol method for NO_2 was operated for UNC smog chamber experiments conducted from October 4 to 18, 1984[7]. The Laser instrument can be operated to monitor two compounds at once. The NO_2 instrument was operated continuously. Several basic experiments were conducted with principal compounds with the goals (1) to obtain data for H_2O_2 (which is rarely measured), and nitric acid (measurements which are almost as rare), (2) to compare formaldehyde data from the laser system with the UNC method, and (3) to obtain low concentration (high sensititivity) formaldehyde data for experiments which often produce formaldehyde concentrations below the reliable detection limits of the UNC method (10 ppb). These last set of experimental conditions include the characterization experiments where NO_2 and HCHO have been observed to off-gas in low concentrations after sunrise.

Table 10. Experiments to Assist Modelers

```
-------------------------------------------------
  Date  CDI HC Ser  Proj Q I P  Sun  Rank
-------------------------------------------------

16-Aug-84 ONI 1A 06    ET 5 4 P  81  Some Problems

      Red Side  0.000 NOx   1.00   ACETALDEHYDE
                      42.00   NITROUS OXIDE
      Blue Side 0.000 NOx   0.98   O3
                      36.00   NITROUS OXIDE

27-Aug-84 ONI 1A 30    ET 7 5 S  92  Best of kind

      Red Side  0.000 NOx   1.00   ACETALDEHYDE
                      80.00   NITROUS OXIDE
      Blue Side 0.000 NOx   1.00   ACETALDEHYDE
                      1.00   O3

16-Sep-84 ONI 1A 30    ET 9 5 S  94  Satisfactory

      Red Side  0.000 NOx   1.00   ACETALDEHYDE
                      50.00   NITROUS OXIDE
      Blue Side 0.000 NOx   1.00   ACETALDEHYDE
                      50.00   NITROUS OXIDE
                      1.00   O3

>>>>> For the Series type of 28 Addition, CO <<<<<

09-Oct-84 ONI 1A 28    ET 9 5 S  69  Best of kind

      Red Side  0.561 NOx   0.96   FORMALDEHYDE
                      50.00   CO
      Blue Side 0.500 NOx   0.96   FORMALDEHYDE
                      0.30   CO
```

Table 10. cont. Experiments to Assist Modelers

Date	CDI	HC	Ser	Proj	Q	I	P	Sun	Rank		
15-Oct-84	ONI	1A	28	ET	9	4	S	89	Satisfactory		
				Red Side	0.021	NOx		1.00	ACETALDEHYDE		
						0.30	CO				
				Blue Side	0.021	NOx		1.00	ACETALDEHYDE		
						50.00	CO				
23-Oct-84	ONI	MC	18	ET	5	5	P	7	Satisfactory		
				Red Side	0.350	NOx		2.00	SYNTHETIC AUTO EXHAUST		
						0.20	FORMALDEHYDE				
				Blue Side	0.350	NOx		2.00	SYNTHETIC AUTO EXHAUST		
						0.20	ISOBUTENE				
20-Aug-85	ONI	MC	26	ET	7	9	P	43	Satisfactory		
				Red Side	0.350	NOx		2.00	SYNURBAN		
						0.20	FORMALDEHYDE				
				Blue Side	0.300	NOx		2.00	SYNURBAN		
						0.80	ISOBUTENE				
23-Aug-85	ONI	MC	26	ET	8	6	P	66	Satisfactory		
				Red Side	0.350	NOx		2.00	SYNURBAN		
						0.20	FORMALDEHYDE				
				Blue Side	0.350	NOx		2.00	SYNURBAN		
						0.20	ISOBUTENE				

Table 10. cont. Experiments to Assist Modelers

Date	CDI	HC	Ser	Proj	Q	I	P	Sun	Rank
04-Oct-84	ONI	10	33	ET	9	5	S	99	Best of kind
Red Side	0.361	NOx	2.07	PROPYLENE					
Blue Side	0.357	NOx	1.02	PROPYLENE					
05-Oct-84	ONI	10	33	ET	9	5	S	70	Best of kind
Red Side	0.365	NOx	3.13	ETHYLENE					
Blue Side	0.370	NOx	1.80	ETHYLENE					
07-Oct-84	ONI	1A	33	ET	8	5	S	45	Best of kind
Red Side	0.005	NOx	0.44	FORMALDEHYDE					
Blue Side	0.005	NOx	1.03	FORMALDEHYDE					
16-Oct-84	ONI	1A	33	ET	8	7	S	59	Satisfactory
Red Side	0.003	NOx	0.42	FORMALDEHYDE					
Blue Side	0.003	NOx	0.25	FORMALDEHYDE					
11-Oct-84	ONI	10	18	ET	9	5	S	80	Satisfactory
Red Side	0.351	NOx	2.86	ETHYLENE					
Blue Side	0.354	NOx	2.25	PROPYLENE					
12-Oct-84	ONI	10	18	ET	9	5	S	80	Satisfactory
Red Side	0.710	NOx	2.68	ETHYLENE					
Blue Side	0.682	NOx	1.96	PROPYLENE					

Table 10. cont. Experiments to Assist Modelers

Date	CDI	HC	Ser	Proj	Q	I	P	Sun	Rank	
23-Aug-84	ONI	1X	18	ET	7	6	P	62	Satisfactory	
	Red Side		0.400	NOx				3.00	METHYLBENZYLQUINONE	
	Blue Side		0.400	NOx				3.00	TRANS-2-BUTENE	
13-Oct-84	ONI	1X	18	ET	8	5	S	91	Some Problems	
	Red Side		0.313	NOx				0.19	HYDROGEN PEROXIDE	
								50.00	CO	
	Blue Side		0.314	NOx				0.10	HYDROGEN PEROXIDE	
								0.30	CO	
14-Oct-84	ONI	1X	18	ET	9	5	S	100	Some Problems	
	Red Side		0.304	NOx				0.40	HYDROGEN PEROXIDE	
	Blue Side		0.307	NOx				0.28	HYDROGEN PEROXIDE	
								50.00	CO	
17-Oct-84	ONI	1X	28	ET	8	6	S	9	Some Problems	
	Red Side		0.304	NOx				0.52	HYDROGEN PEROXIDE	
								50.00	CO	
	Blue Side		0.307	NOx				0.48	HYDROGEN PEROXIDE	
19-Jul-85	CNI	1X	33	ET	8	2	P	98	Satisfactory	
	Red Side		0.000	NOx				1.00	BIACETYL	
	Blue Side		0.000	NOx				3.00	BIACETYL	
11-Sep-85	oni	1P	28	ET	7	7	P	43	Satisfactory	
	Red Side		0.350	NOx				3.00	BUTANE	
	Blue Side		0.350	NOx				3.00	BUTANE	
								50.00	CO	

Background-Air Chamber Experiments

A background-air chamber experiment was performed on October 6, 1984. The Unisearch instrument can detect sub-ppb concentrations. The instrument was set to monitor formaldehyde and H_2O_2.The instrument experienced technical problems in the morning. However by 1045 EDT the instrument seemed to be operating. From this time to 1345 EDT, formaldehyde levels in both sides increased from 6 to 11 ppbC. Measurements were continued from 1615 to 1815 EDT during which time formaldehyde concentrations measured remained generally constant (9 to 12 ppbC). H_2O_2 measurements were also taken during the same time periods. Between 1045 to 1345 EDT approximately 1 ppb (ranging from 0.7 to 1.7 ppb) was measured. From 1615 to 1815 EDT the concentrations ranged from 1.5 to 3.4 ppb. The Luminol NO_2 measurements were about 3 ppb in the morning on both sides while the UNC Bendix Chemiluminescence NO_2 measurements were about 5 to 7 ppb both sides. The UNC instrument showed that NO_2 decreased by 1 ppb in the RED side and increased in the BLUE side to 10 ppb by 1120 EDT while the Luminol monitor showed an increase to 6 ppb in both sides: the two monitors agree in the delta NO_2 for the BLUE side and disagree with the RED even in the shape of the time-concentration profile. Perhaps the sample switching valve was not operating and the Luminol data are really for the BLUE side only.

On October 8, no experiment was performed. The experiment performed the day before was a 1 vs 0.5 ppm HCHO decay experiment with no NO_x injected. The chamber was vented all day. The Unisearch instruments were however monitoring the chamber. Formaldehyde, H_2O_2, and NO_2 were monitored continuously. Starting at midnight, there was about 5 ppb of HCHO in the BLUE side and about 3 ppb in the RED. The HCHO concentrations on both sides decreased to about 1 ppb on both sides by dawn. No formaldehyde data were taken from 645 until 1045 EDT, except for one reading on the BLUE side at 0845 EDT (0.7 ppb). At 1045 to 1215 EDT, the measurements showed about 5 to 6 ppb HCHO in BLUE and 3 to 4 ppb in RED. Again no data were taken until 1915 EDT, where measurements showing just over 1 ppb were made for each side. Luminol NO_2 measurements made between 0800 and 1200 EDT on both sides showed about 1 to 2 ppb in RED and 2 to 4 ppb in BLUE. Measurements were 0.3 ppb after 2000 EDT on both sides until midnight. Measurements with the UNC monitors were not made.

Aldehyde Decay Chamber Experiments

Four aldehyde experiments were conducted with the Unisearch analytical methods. A 1 vs 0.5 ppm formaldehyde decay (no NO_x injected) was conducted on

October 7. A matched formaldehyde and NO_x run with 50 ppm CO added to one side was conducted on October 9. This was a two-day run. A matched acetaldehyde with no injected NO_x, but with 50 ppm CO added to one side, was conducted on October 15. Another 1 vs 0.5 ppm formaldehyde decay (no NO_x injected) was conducted on October 16.

For the October 7 experiment, the formaldehyde data from both analytical methods agree fairly well (see Figure 17). The H_2O_2 data showed initial concentrations of 0.5 to 1 ppb (both sides) with an increase to a maximum value of 12 ppb for the 1 ppm HCHO side and to 3 ppb on the lower HCHO side by 1345 EDT. The Luminol NO_2 data shows initial concentrations of 0.5 ppb both sides increasing to 51 ppb on the BLUE side and 21 ppb on the RED side, near noon. The UNC NO_2 data shows initial values of 1.5 ppb RED and 5 ppb BLUE, increasing to only 4 ppb on RED side and about 7.5 ppb on BLUE side by noon. We feel that the UNC Bendix NO_x monitor would have easily monitored an NO_2 increase to 20 and especially 50 ppb. HNO_3 was not measured this day.

Starting early October 9 a two-day experiment, with target initial conditions of matched 1 ppm HCHO and 0.5 ppm NO_x, with 50 ppm of CO added to the RED side, was started. The UNC monitor measured an initial HCHO concentration of 0.96 ppm while the Unisearch method reported 0.77 to 0.78 ppm, about 19 percent less than the UNC measurement. Unisearch measurements were made only between 715 and 815 EDT and after 2000 EDT the first day and through most of the second day. The measurements made from 2000 to 0700 EDT the next morning show the stability of HCHO in the dark. At 2000 EDT the BLUE concentration was about 91 ppb and the RED about 104 ppb. By morning the BLUE concentration was about 70 ppb and the RED about 72 ppb. See Figure 18. The Luminol NO_2 measurements appear to be much higher than the UNC measurements. H_2O_2 measurements were only made between 915 to 1845 EDT the first day (with a few missing values indicated between 1045 and 1345 EDT). The highest measurements were about 3 ppb between 915 and 1015EDT, decreasing to 1 ppb and less after noon. HNO_3 measurements were made between 715 EDT and midnight the first day and from 745 to 1445 EDT the second day. The morning measurements on the first day were about 1 ppb, increasing after 0900, maximizing at 30 ppb on the BLUE side about 1430 EDT and 23 ppb on the RED side about the same time. Concentrations decreased steadily to about 3 ppb by midnight. By 0715 EDT the next morning, the HNO_3 measurements ranged from 1 to 3 ppb (some noise) increasing to only about 4 to 5 ppb about noon and remaining at this level until 1500 EDT (see Figure 18). Much less HNO_3 and H_2O_2 was observed than would be expected based upon theory. We believe part of the prob-

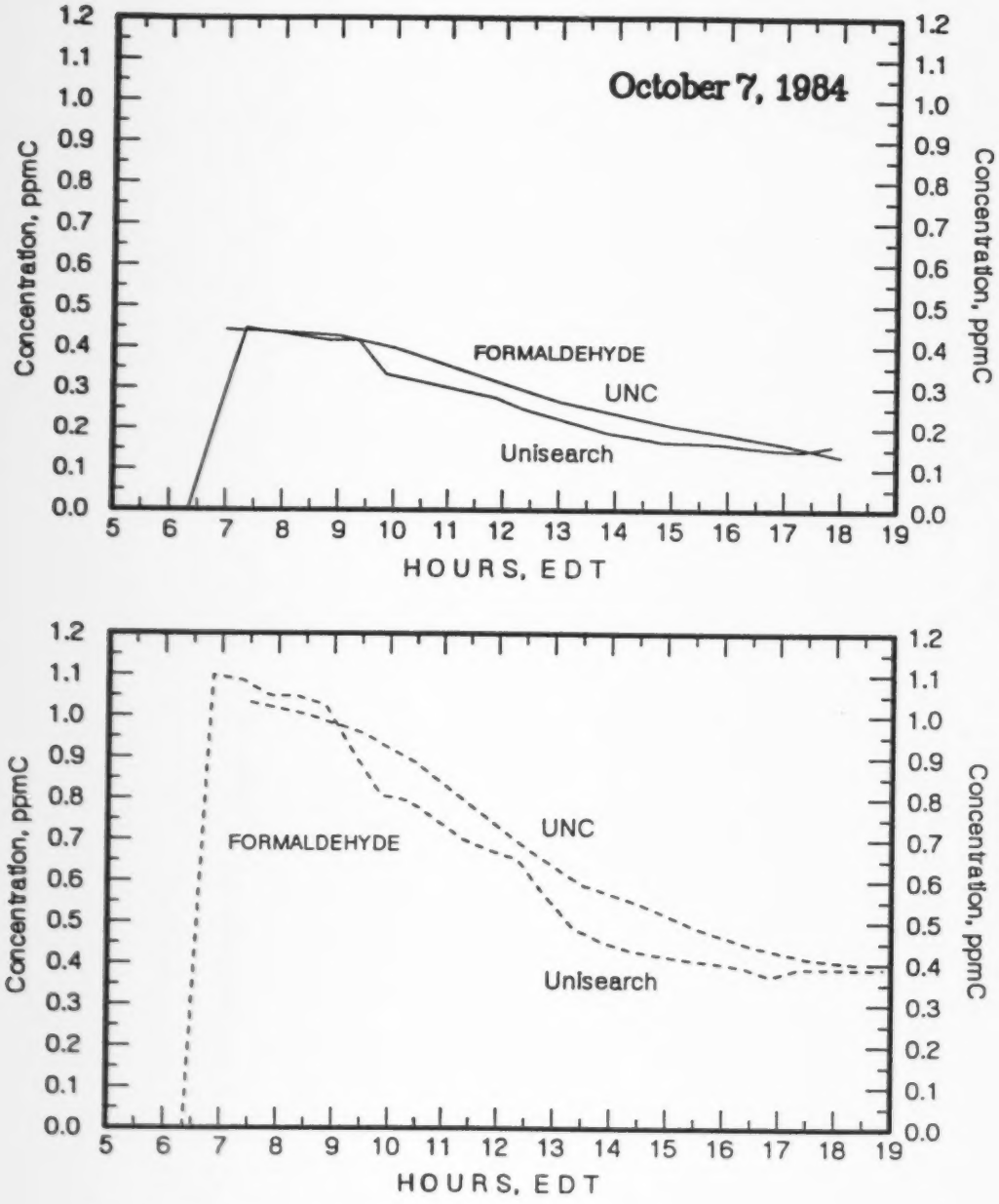

Figure 17. 1.03 vs. 0.44 ppmC Formaldehyde only (UNC and Unisearch Data).
Top: (Solid) 0.44 ppmC Formaldehyde;
Bottom: (Dashed) 1.03 ppmC Formaldehyde;

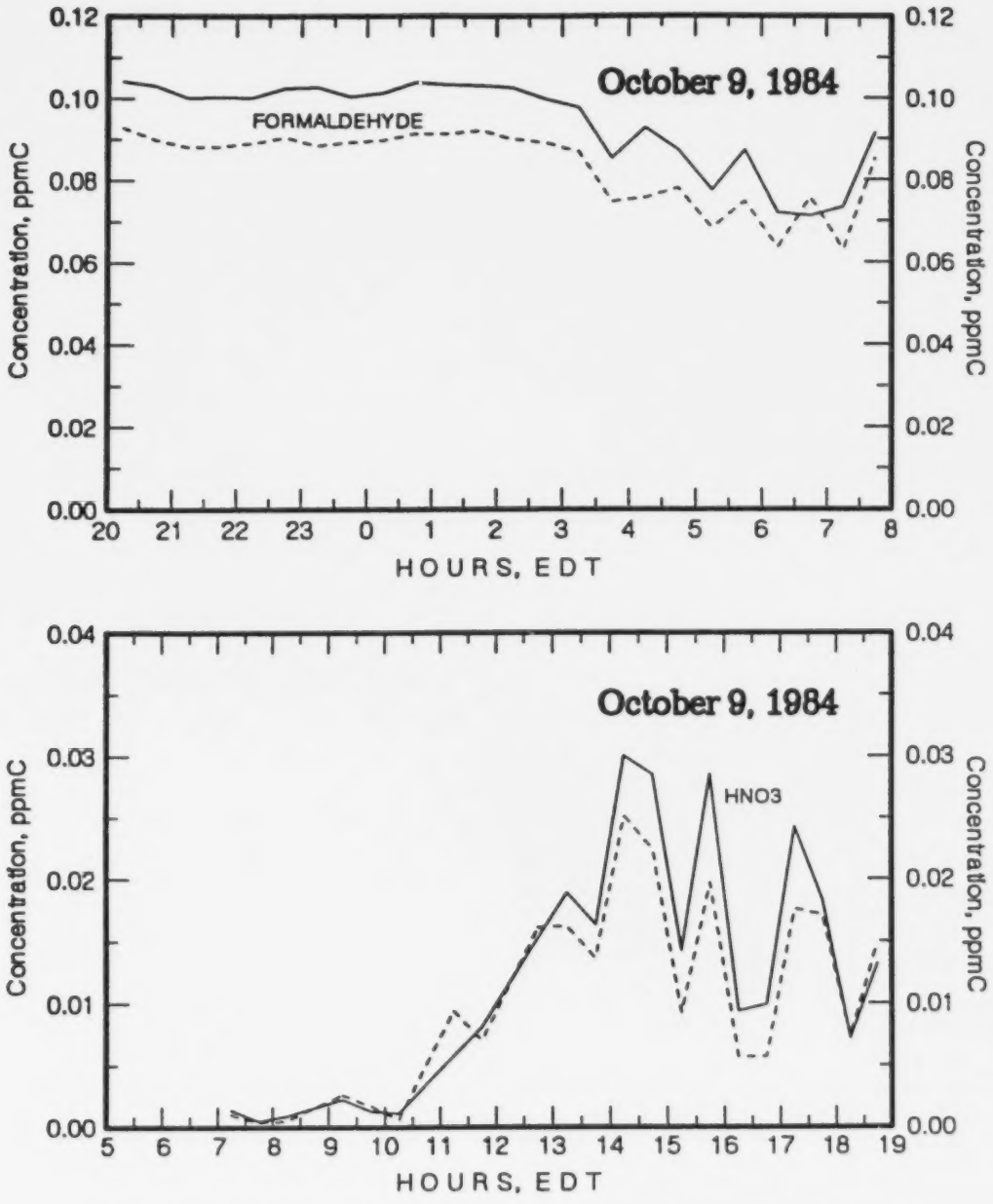

Figure 18. Matched 0.96 ppmC Formaldehyde and 0.5 ppm NO_x; 50 ppm CO (solid)
Top: Night-time (after first day irradiation) Formaldehyde Data (Unisearch).
Bottom: First-day HNO_3 Data (Unisearch).

lem with the lower concentrations of these compounds, (especially HNO_3 since we have measured much higher concentrations of this species under warm dry conditions) is that the cooler October conditions result in greater wall losses. Even though the chamber was dehumidified, the minimum dewpoint acheivable by the air-conditioning coils is close to the initial morning temperature; if the air in the morning is near saturation, it is more difficult (takes longer) to dehumidify the chamber.

On October 15, (matched acetaldehyde, CO added one side) very little data were taken with the Unisearch instruments. HNO_3 and H_2O_2 data were taken for only 3.5 hours (1.5 in morning; 2 from 1415 to 1615 EDT), HCHO was taken only after the run (venting started) until midnight. NO_2 data was taken from midnight before the run (during chamber drying) until 915 EDT. Evidience of NO_2 off-gassing was seen. NO_2 off-gassing was also detected by the UNC method but to a lesser extent. PAN measurements made by the UNC ECD method agree fairly well with the chemiluminescent UNC NO_2 measurements. This is expected because of the large initial acetaldehyde concentrations.

On October 16 a HCHO – only (no injected NO_x) decay experiment was conducted. The Unisearch instrument was not operating for HCHO in the morning to obtain initial conditions, or time-concentration profile data until 1045 EDT. In general the Uniserarch data was about 10 to 20 percent lower than the UNC data before noon and 25 to 50 percent lower by the end of the run. No other Unisearch data was reported for this experiment.

Propylene, Ethylene and NOx Chamber Experiments

Propylene and ethylene, NO_x experiments were conducted on four days: Oct 4, 5, 11, and 12. The earlier runs experienced more down time for the Unisearch equipment probably since the instruments were not setup and turned on until October 3.

On the 11th, 3 ppmC ethylene was compared with 2 ppmC of propylene with matched target NO_x initial conditions. The formaldehyde data from the Laser system were always lower (anywhere from 50 to 30 percent) than the UNC data. Timing was somewhat different also. The calibration factors for the UNC data were very consistent from Oct 5 to this time. Formaldehyde measurements with the UNC method for the ethylene sides of the experiments performed on the 5th and the 11th were very similar at noon (light similar from morning to noon) and about 150 ppb higher on the 5th than the 11th perhaps since the afternoon light

on the 5th was poorer. Consequently less HCHO photolyzed allowing more to accumulate. See Figure 19. The Unisearch report does not include calibration information; we do not know how stable the calibration (or instrument response) was during this time period, but the Unisearch measurements for the similar ethylene and propylene runs conducted on October 4, 5, and 11 were consistent. The HNO_3 data were always below 30 ppb.

During the October 12th experiment, which was a repeat of the October 11th experiment, H_2O_2 was monitored instead of HCHO . Less then 10 ppb was observed in either side. HNO_3 was also monitored. Again, not quite 30 ppb was observed.

Hydrogen Peroxide

Three experiments were conducted with target conditions of NO_x and high concentrations of H_2O_2 which were injected before dawn. In these experiments, 50 ppm of CO was added to one side. One of the reasons for these experiments was to determine if H_2O_2 could be injected into the chamber. Several techniques were tried.

On October 13, a 0.33 ml aliquot of 30 percent H_2O_2 was placed into the return manifolds to the smog chambers. The Unisearch monitor saw an increase immediately in the chamber which increased steadily with time. It was clear that hours were needed to achieve a stable concentration and less than the quantitative amount was detected in the chamber.

On October 14, the injections were increased (1.07 ml), starting much earlier (0300 EDT). The data show continued evaporation and build-up of H_2O_2 after sunrise to 0.72 ppm in RED (0845 EDT) and 0.63 ppm in BLUE (0915 EDT). The concentrations then began to decrease with a half-life of about 3 hours. See Figure 20. The side with the high CO made over 0.2 ppm O_3 while the side without the CO still had 0.2 ppm of NO by the end of the run. See Figure 20.

On October 17, another injection method was tried. An aliquot (0.3 ml) of 30 percent hydrogen peroxide was placed on a watchglass on top of an insulated beaker of hot water (heat source to encourage evaporation). The beakers were placed inside each side of the chambers about 0230 EDT. By 0500, 0.52 ppm H_2O_2 was in the RED side and 0.48 ppm in the BLUE side. Since this was still less than the quantitative amount, additional aliquots were placed inside the return manifolds to the smog chambers, in an attempt to reach the target concentrations of 1 ppm. Clearly there are problems with either injection of H_2O_2 or there are large losses of H_2O_2 that are not explained by current gas phase kinetics. Perhaps

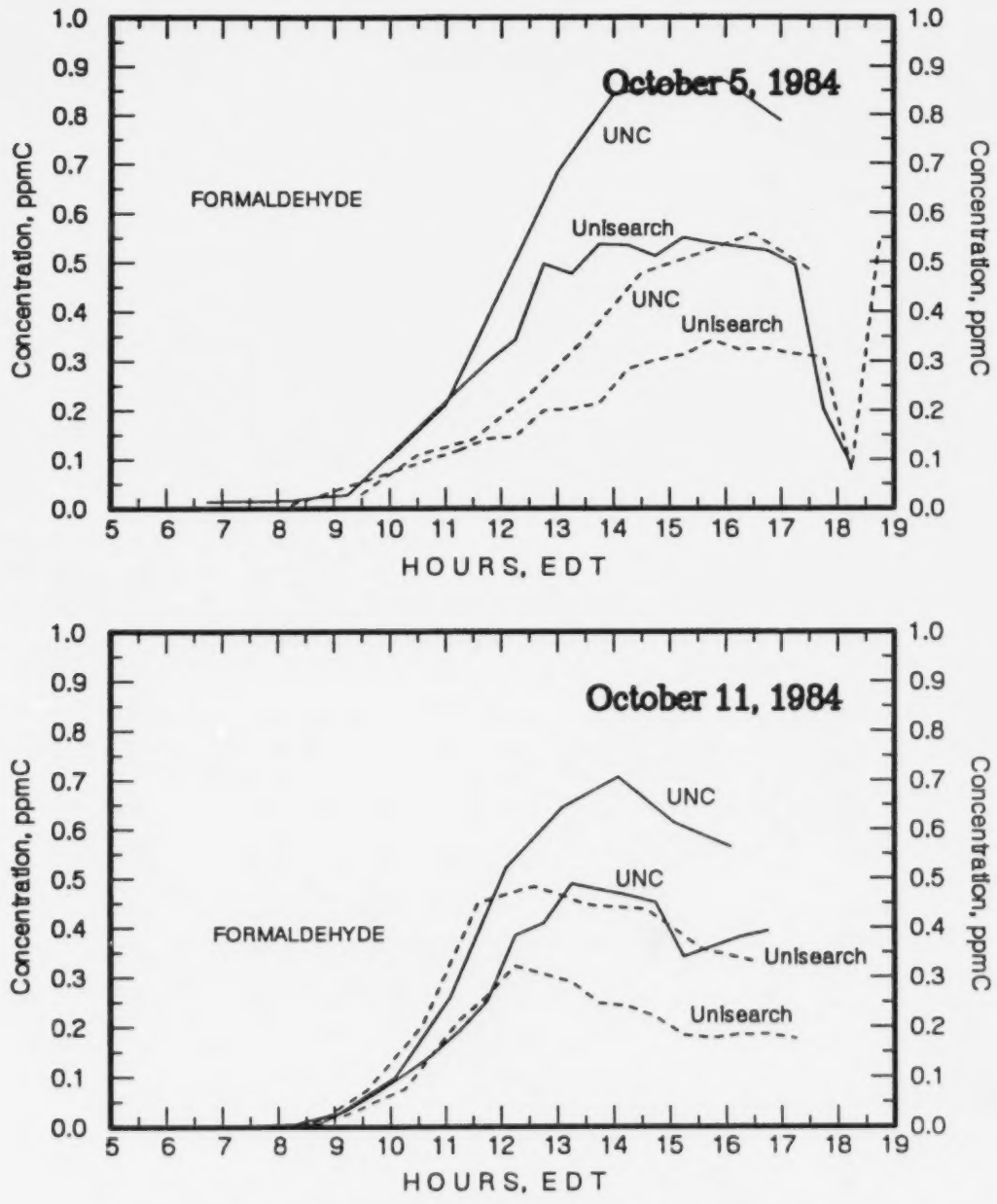

Figure 19. Comparison of UNC and Unisearch Formaldehyde Data.
Top: (Solid) 3.1 ppmC Ethylene, 0.35 ppm NO_x;
(Dashed) 1.8 ppmC Ethylene, 0.35 ppm NO_x;
Bottom: (Solid) 2.9 ppmC Ethylene, 0.35 ppm NO_x;
(Dashed) 2.3 ppmC Propylene, 0.35 ppm NO_x;

the chamber walls are large sinks for H_2O_2. In any case, although H_2O_2 data were collected in some of the October experiments, they are probably not suitable for modeling.

Aromatic Oxidation Products

An experiment conducted on August 23, 1984 was an attempt to study the reactivity of a proposed toluene oxidation product identified by mass spectroscopy, from the dissertation work of Mike Gery: methylbenzylquinone (MBQ). 3 ppmC was injected into the chamber along with 0.4 ppm NO_x. Because MBQ was thought to be highly reactive, 3 ppmC of trans-2-butene was injected on the other side along with the same NO_x concentration. Figure 21 shows the NO_x and O_3 profiles. Figure 22 shows the profiles of the two hydrocarbons. Although the MBQ decays rather quickly (but not nearly as fast as t-2-butene), it does not oxidize the NO_x fast enough to generate much O_3.

Isobutene As Surrogate For HCHO

Isobutene has been used as a surrogate for formaldehyde in some other studies. The August 23, 1985 experiment is one of several carried out to test whether or not isobutene is an appropriate surrogate. Both sides contained 0.35 ppm NO_x , and 2 ppmC of SynUrban. One side had 0.2 ppmC of HCHO and the other side had 0.2 ppmC of isobutene. The HCHO side was more reactive. $NO - NO_2$ crossover occured about 50 minutes sooner on the HCHO side amd the O_3 yield was about 50 percent greater. The results are shown in Figure 23. Unfortunately the HCHO instrument was not operational. The initial concentration is based on the weight of the paraformaldehyde injected and the chamber temperature. Two other similar experiments were conducted on October 23, 1984 and August 20, 1985. The October 23rd experiment was similar to the August 23rd experiment except that the base HC was SynAuto. Although the light was very poor for this experiment, the outcome was consistent with August 23, 1985. The August 20th experiment was similar to the August 23th except that the isobutene was increased to 0.8 ppmC. In this case the isobutene side was more reactive.

Ozone Photolysis

Gary Whitten of Systems Applications Inc. suggested an experiment which can be used to study the photolysis rate of O_3. Both sides are injected with nitrous oxide (N_2O) in excess (about 50 pounds or 81,000 ppm). A large concentratrion of

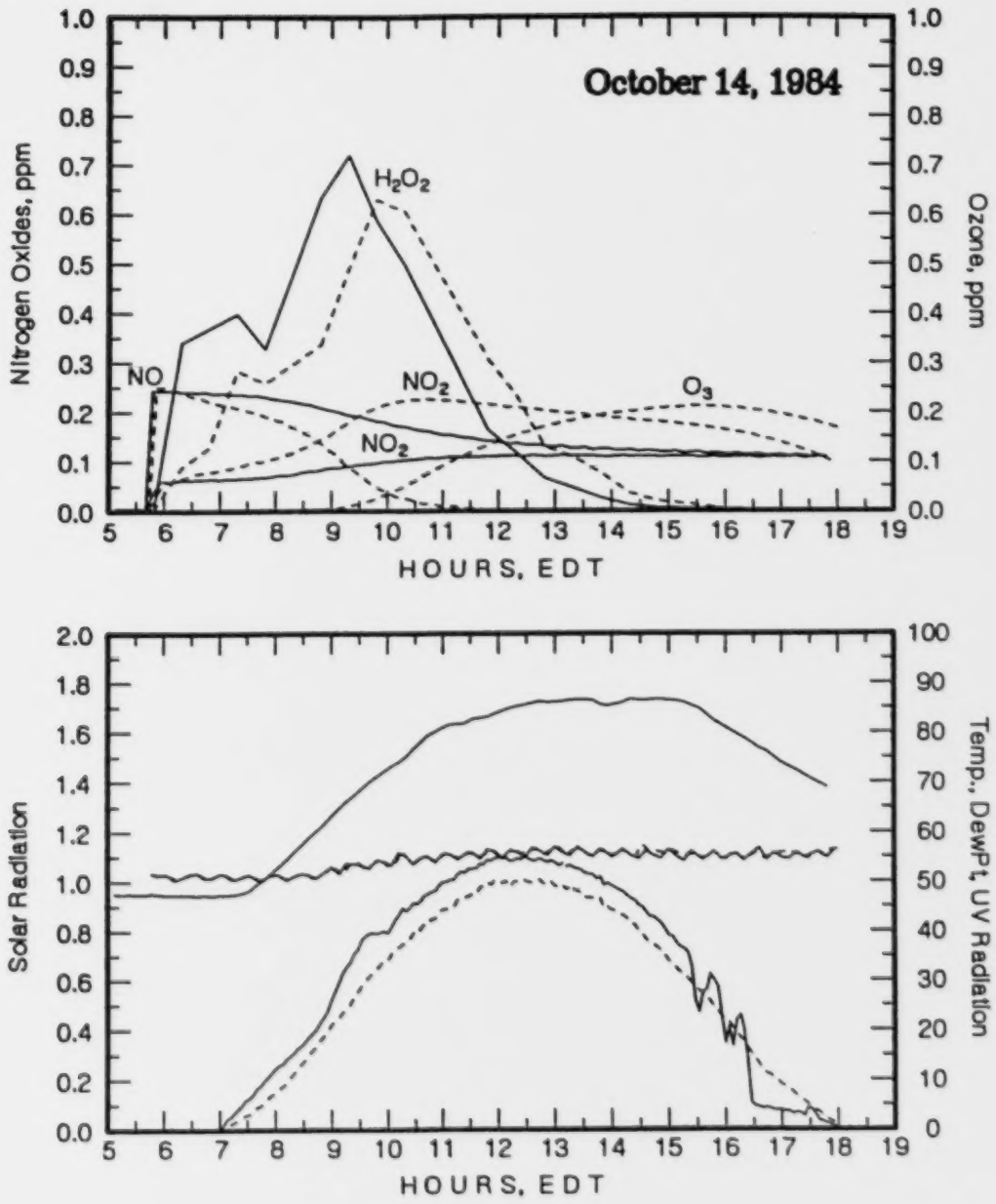

Figure 20. Hydrogen Peroxide and NO_x.
Top: (Solid) "0.4 " ppm H_2O_2;
(Dashed) "0.3" ppm H_2O_2;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line, mcal-cm^{-2}-sec^{-1});

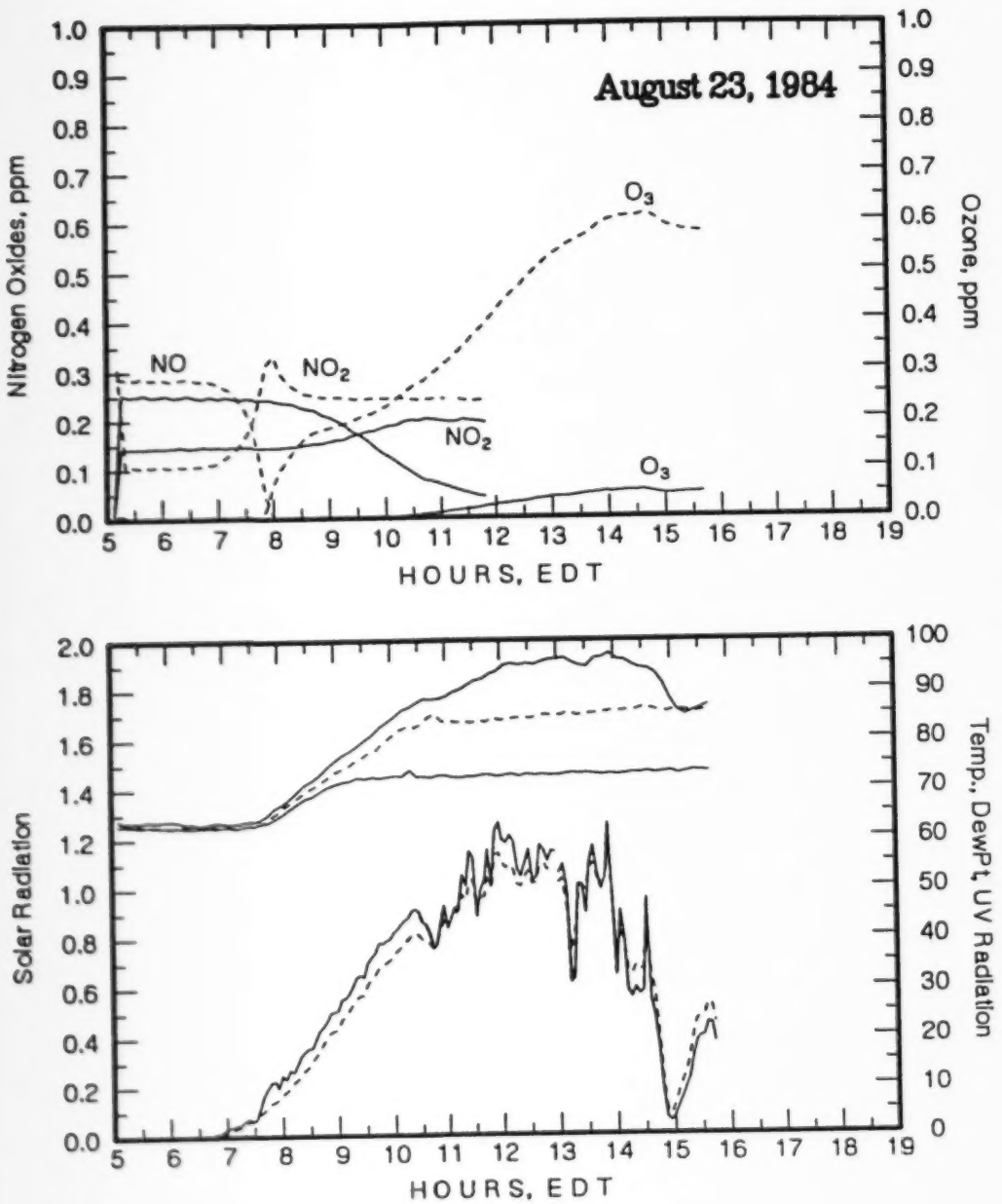

Figure 21. Methylbenzylquinone vs. t-2-butene;
Top: (Solid) 3.0 ppmC Methylbenzylquinone;
(Dashed) 3.1 ppmC t-2-butene;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line, mcal-cm^{-2}-sec^{-1});

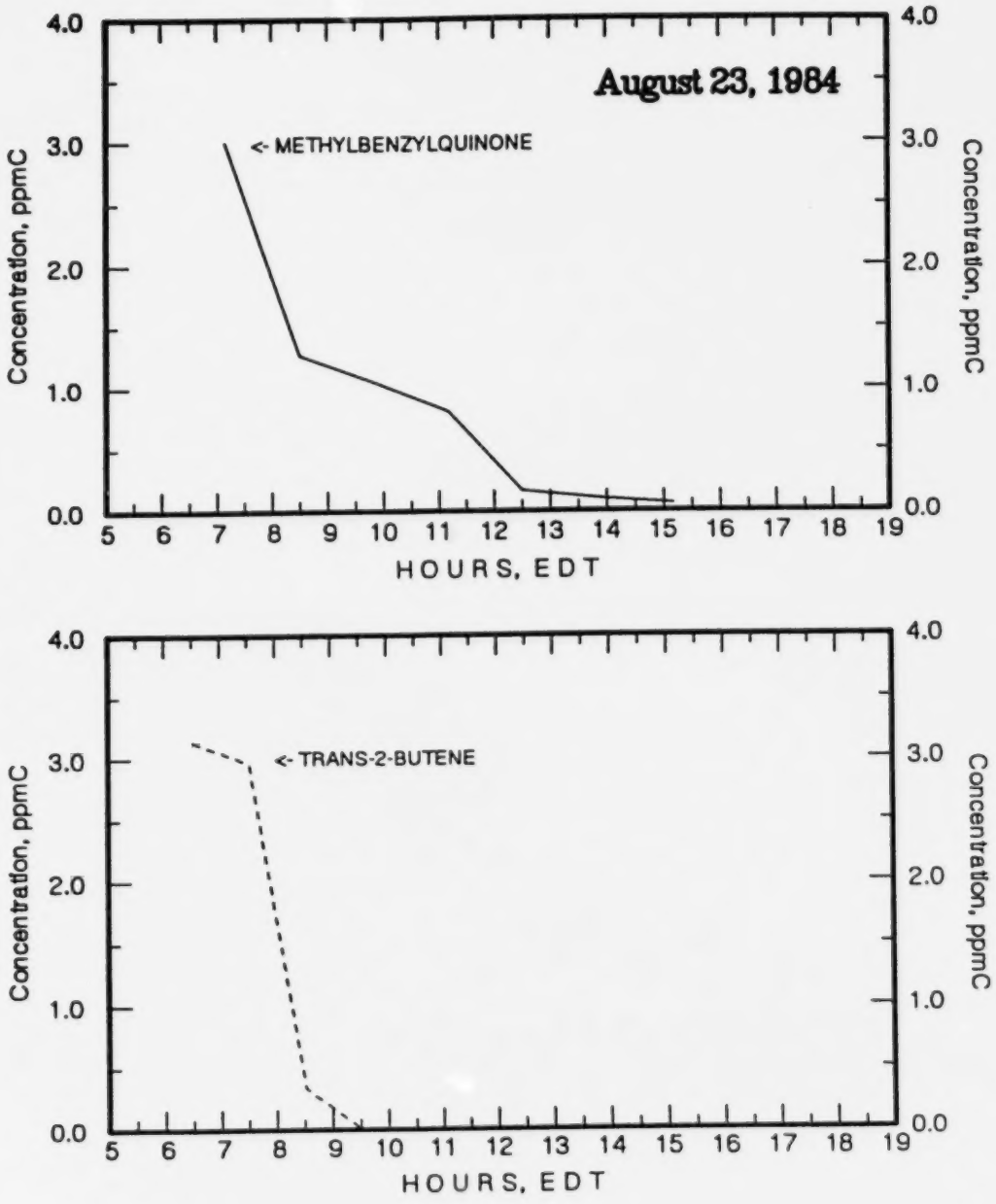

Figure 22. Methylbenzylquinone vs. t-2-butene;
Top: (Solid) 3.0 ppmC Methylbenzylquinone;
Bottom: (Dashed) 3.1 ppmC t-2-butene;

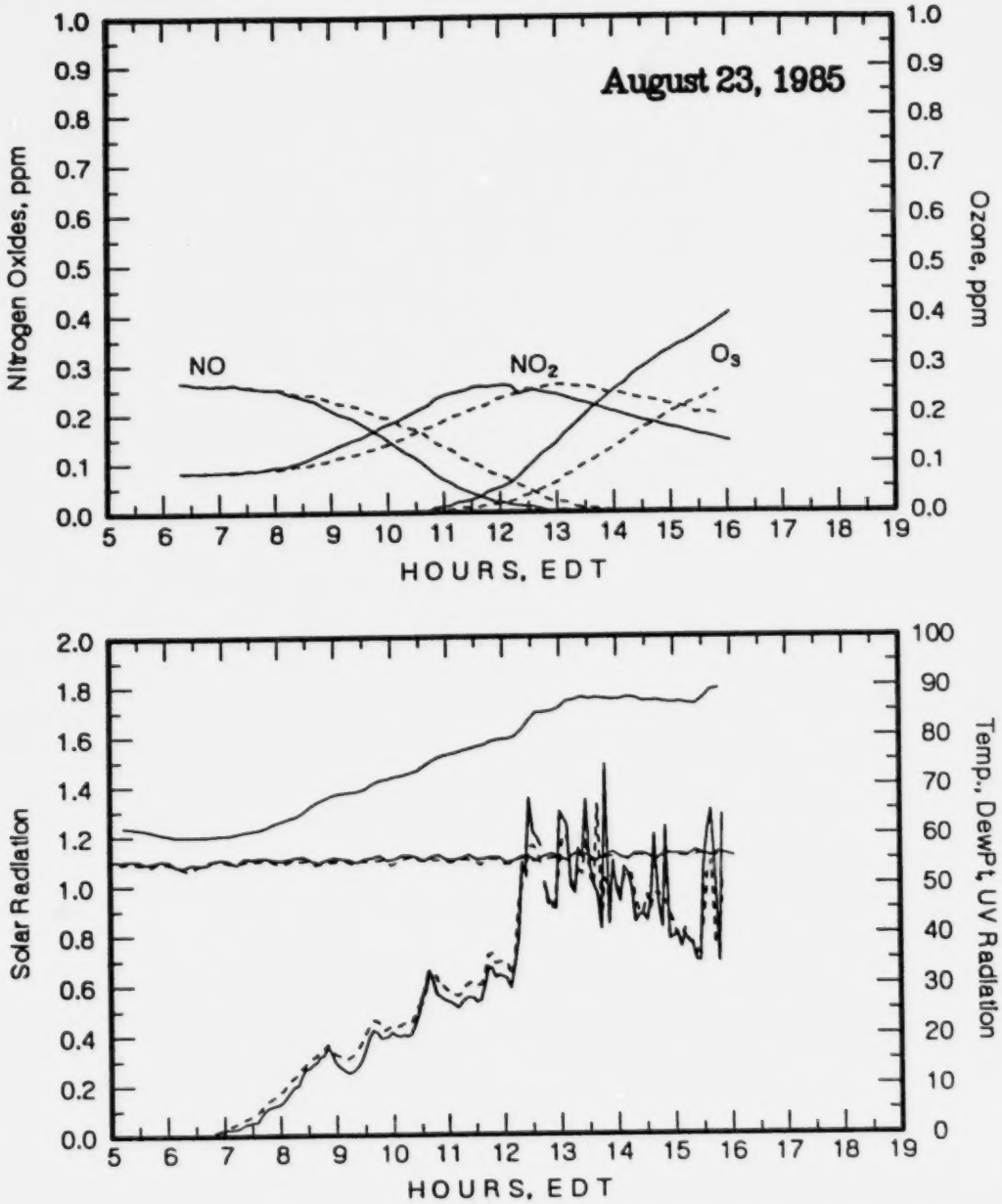

Figure 23. 0.2 ppmC Isobutene vs. 0.2 ppmC Formaldehyde; Matched SYNURBAN;
Top: (Solid) 0.2 ppmC Formaldehyde; 2.0 ppmC SYNURBAN;
(Dashed) 0.2 ppmC Isobutene; 2.0 ppmC SYNURBAN;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line, mcal-cm^{-2}-sec^{-1});

O_3 is injected into one side. O_3 photolysis yields O1d which reacts with the N_2O to produce NO (or N_2) which can be monitored as NO or actually as NO_2 since O_3 is present. 1 ppmC of acetaldehyde is also injected into both sides. Any NO_2 formed in either side will therefore be converted to PAN which can be detected on the gas chromatograph/ ECD system as well as on the Bendix NO_x analyzer as NO_2. The side without the injected O_3 is used to estimate the background NO_x off–gassing and other chamber artifacts. The September 16, 1984 results of experiment is shown in Figure 24 and Figure 25.

Routine Experiments To Assist Modelers

Certain experiments are performed to assist modelers. These include the routine "chamber characterization" experiments such as:

- Background Air Only
- NO_x only
- NO_x with CO added to one side
- O_3 decay
- NO_2 and O_3 at night
- Aldehyde only
- Aldehyde with CO added to one side.

Matched propylene experiments are also rountinely conducted, which provide well studied experiments to test chamber assumptions and conditions which have been repeated many times through the years, and which allow modelers to detect peculiarities in results or modeling assumptions. Other matched runs which demonstrate the ability to match reactivity in the two chamber sides are also conducted. These are listed in Table 11.

Sun Position, Site and Structure Effects On Chamber

Measurements were made of the chamber and grounds and were represented in a coordinate system (see Figure 26) to study the possible effect on the chamber from surrounding structures and vegetation. Measurements of light (UV and total solar radiation) were made concurrently both inside and outside the chamber. Figure 27 shows the inside and outside measurements made with the Eppley Total Solar Radiation (TSR) and ultraviolet (UV) radiometers on October 9, 1985. As can be seen, the UV is attenuated more than the TSR. The TSR seems to be

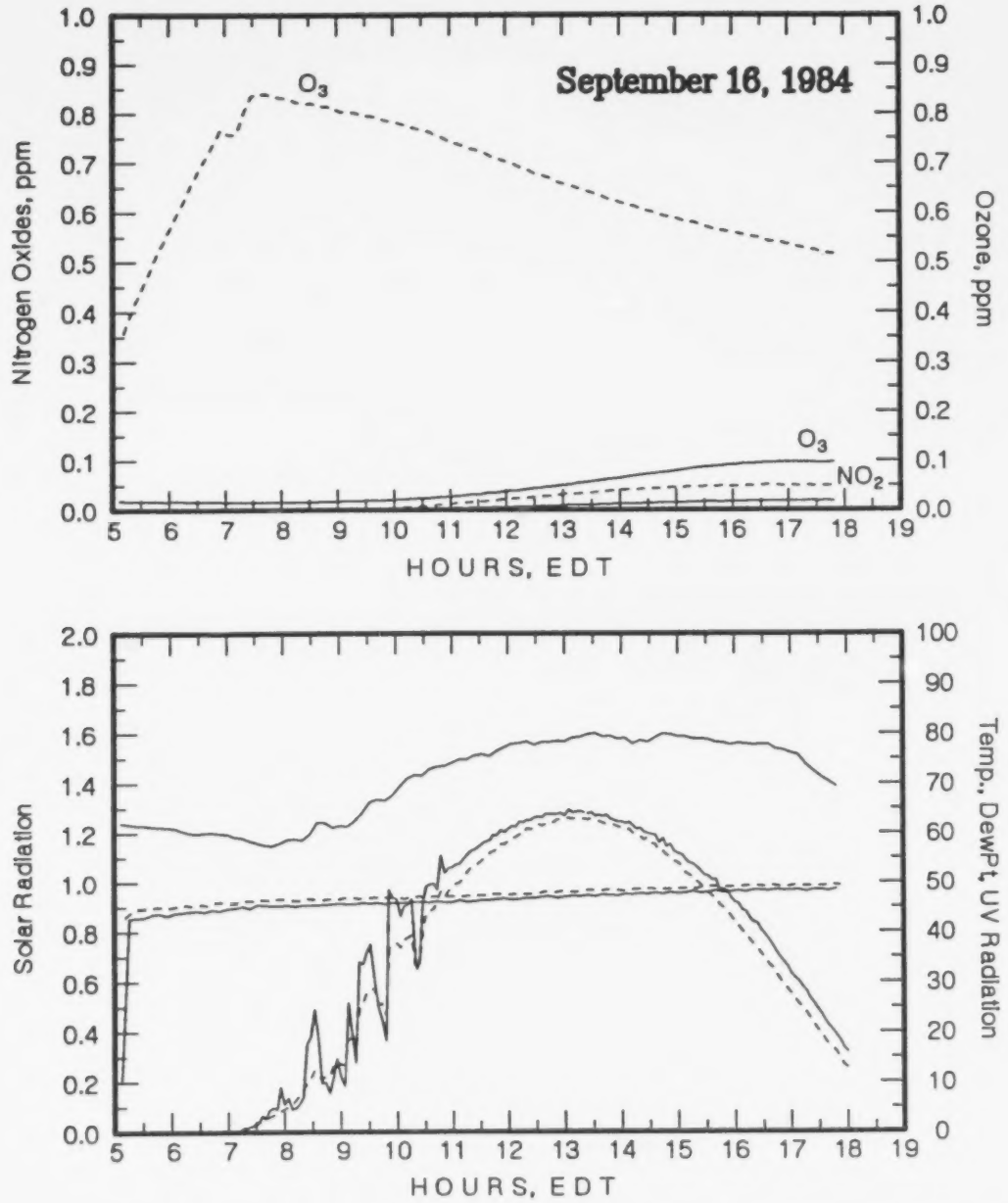

Figure 24. 81,000 ppm N_2O and 1 ppmC Acetaldehyde both; 0.84 ppm O_3 (dashed).
Top: (Solid) 81,000 ppm N_2O and 1 ppmC Acetaldehyde;
(Dashed) 81,000 ppm N_2O, 1 ppmC Acetaldehyde, and 0.84 ppm O_3;
Bottom: RED chamber air temperature (top solid line, °F);
RED (solid line) and BLUE (dashed line) chamber dewpoint (°F);
ambient total solar radiation (solid line, cal-cm^{-2}-sec^{-1});
ambient ultraviolet radiation (dashed line, mcal-cm^{-2}-sec^{-1});

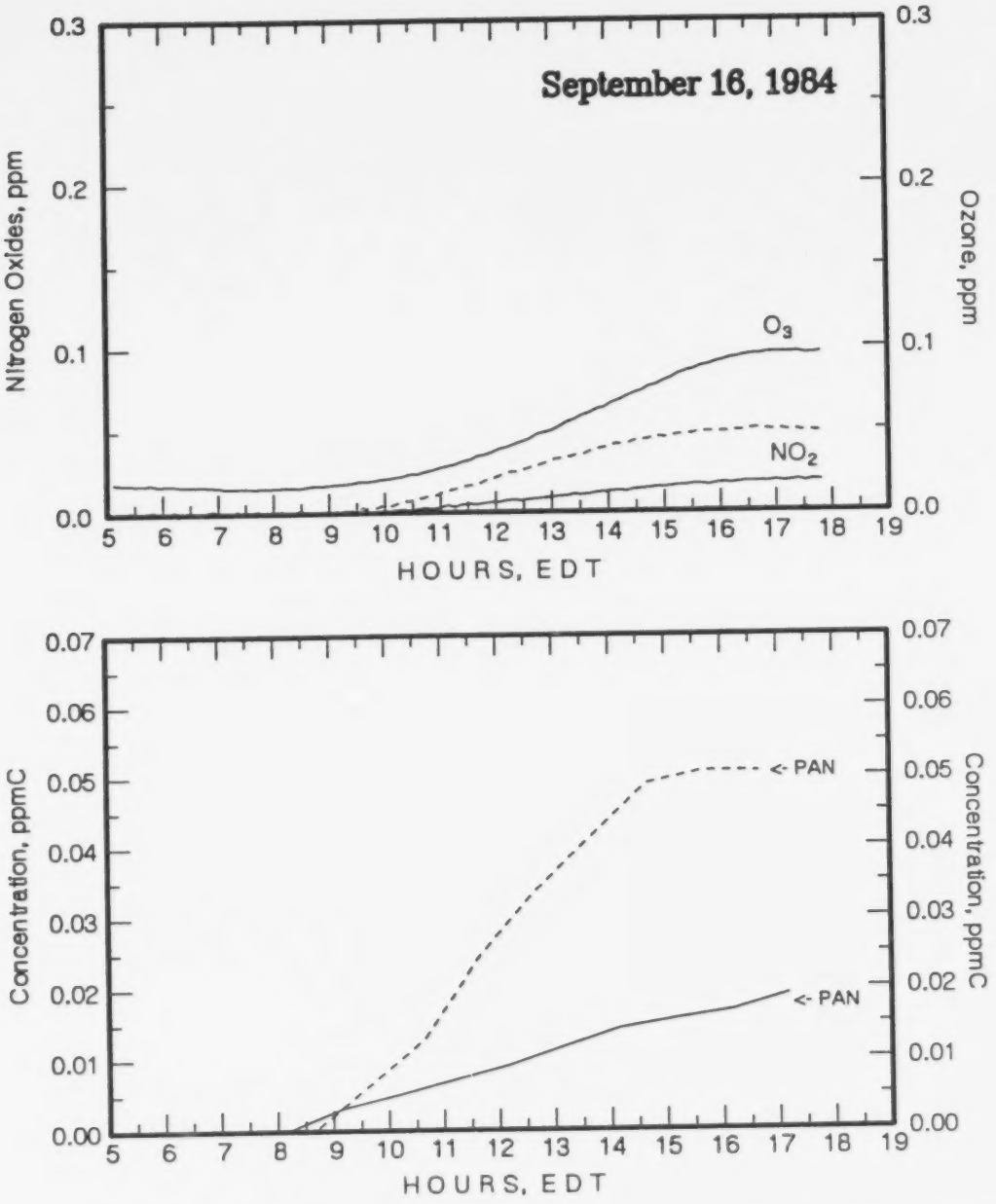

Figure 25. 81,000 ppm N_2O and 1 ppmC Acetaldehyde both; 0.84 ppm O_3 (dashed).
Top: (Solid) 81,000 ppm N_2O and 1 ppmC Acetaldehyde;
(Dashed) 81,000 ppm N_2O, 1 ppmC Acetaldehyde, and 0.84 ppm O_3;
Bottom: PAN Data.

Table 11. Routine Experiments to Assist Modelers

Date	CDI	HC	Ser	Proj	Q	I	P	Sun	Rank
11-Jul-84	ONI	1A	09	ET	8	8	P	81	Satisfactory
	Red Side	0.500	NOx	1.00	FORMALDEHYDE				
	Blue Side	0.500	NOx	1.00	FORMALDEHYDE				
>>>>> For the Series type of 07 Matched propylene <<<<<									
19-Aug-84	ONI	10	07	ME	3	3	P	76	Satisfactory
	Red Side	0.350	NOx	3.00	PROPYLENE				
	Blue Side	0.350	NOx	3.00	PROPYLENE				
20-Aug-84	ONI	10	07	ME	9	4	P	92	Satisfactory
	Red Side	0.350	NOx	3.00	PROPYLENE				
	Blue Side	0.350	NOx	3.00	PROPYLENE				
30-Aug-84	CNI	10	70	ME	5	4	P	83	Satisfactory
	Red Side	0.350	NOx	2.00	PROPYLENE				
	Blue Side	0.350	NOx	2.30	PROPYLENE				
18-Sep-84	ONI	10	33	ME	8	4	P	49	Best of kind
	Red Side	0.500	NOx	4.0	PROPYLENE				
	Blue Side	0.250	NOx	2.0	PROPYLENE				

Table 11. cont. Routine Experiments to Assist Modelers

Date	CDI	HC	Ser	Proj	Q	I	P	Sun	Rank
03-Oct-84	CNI	10	07	ET	6	5	P	97	Best of kind
Red Side	0.350	NOx	2.00	PROPYLENE					
Blue Side	0.350	NOx	2.00	PROPYLENE					
08-Jul-85	ONI	10	07	ME	7	6	P	90	Best of kind
Red Side	0.500	NOx	1.50	PROPYLENE					
Blue Side	0.500	NOx	1.50	PROPYLENE					
16-Aug-85	ONI	10	07	ME	8	5	P	60	Satisfactory
Red Side	0.500	NOx	1.50	PROPYLENE					
Blue Side	0.500	NOx	1.50	PROPYLENE					
06-Sep-85	CNI	10	07	ME	7	7	P	97	Satisfactory
Red Side	0.500	NOx	3.51	PROPYLENE					
Blue Side	0.500	NOx	3.51	PROPYLENE					
Number of runs of this series is 2									
>>>>> For the Series type of 01 Characterization; Background <<<<<									
06-Sep-84	CNI	B	01	ME	8	0	P	85	Best of kind
Red Side	0.0	NOx	0.00	BACKGROUND					
Blue Side	0.0	NOx	0.00	BACKGROUND					
06-Oct-84	CNI	B	01	ET	9	4	S	53	Best of kind
Red Side	0.018	NOx	0.00	BACKGROUND					
Blue Side	0.019	NOx	0.00	BACKGROUND					
Number of runs of this series is 2									

Table 11. cont. Routine Experiments to Assist Modelers

```
-------------------------------------------------
  Date  CDI HC Ser  Proj Q I P  Sun  Rank
-------------------------------------------------

>>>>> For the Series type of 03 Characterization; NOx oxid. CO added <<<<<

28-Aug-85 CNI B  03   ME 7 8 P  54  Satisfactory

      Red Side  0.500 NOx  50.00   CO

Number of runs of this series is 1

>>>>> For the Series type of 08 Matched mixture <<<<<

07-Jul-84 ONI MC 08   ET 5 5 P  68  Satisfactory

      Red Side  0.350 NOx   3.00   UNCMIX
      Blue Side 0.350 NOx   3.00   UNCMIX

25-Oct-84 ONI 1P 28   ET 5 5 P  38  Satisfactory

      Red Side  0.350 NOx   3.00   BACKGROUND
                      50.00   CO
      Blue Side 0.350 NOx   3.00   BACKGROUND

26-Oct-84 TNI 1A 28   ET 5 5 P  42  Satisfactory

      Red Side  0.000 NOx   1.00   ACETALDEHYDE
                      50.00   CO
      Blue Side 0.000 NOx   1.00   ACETALDEHYDE
```

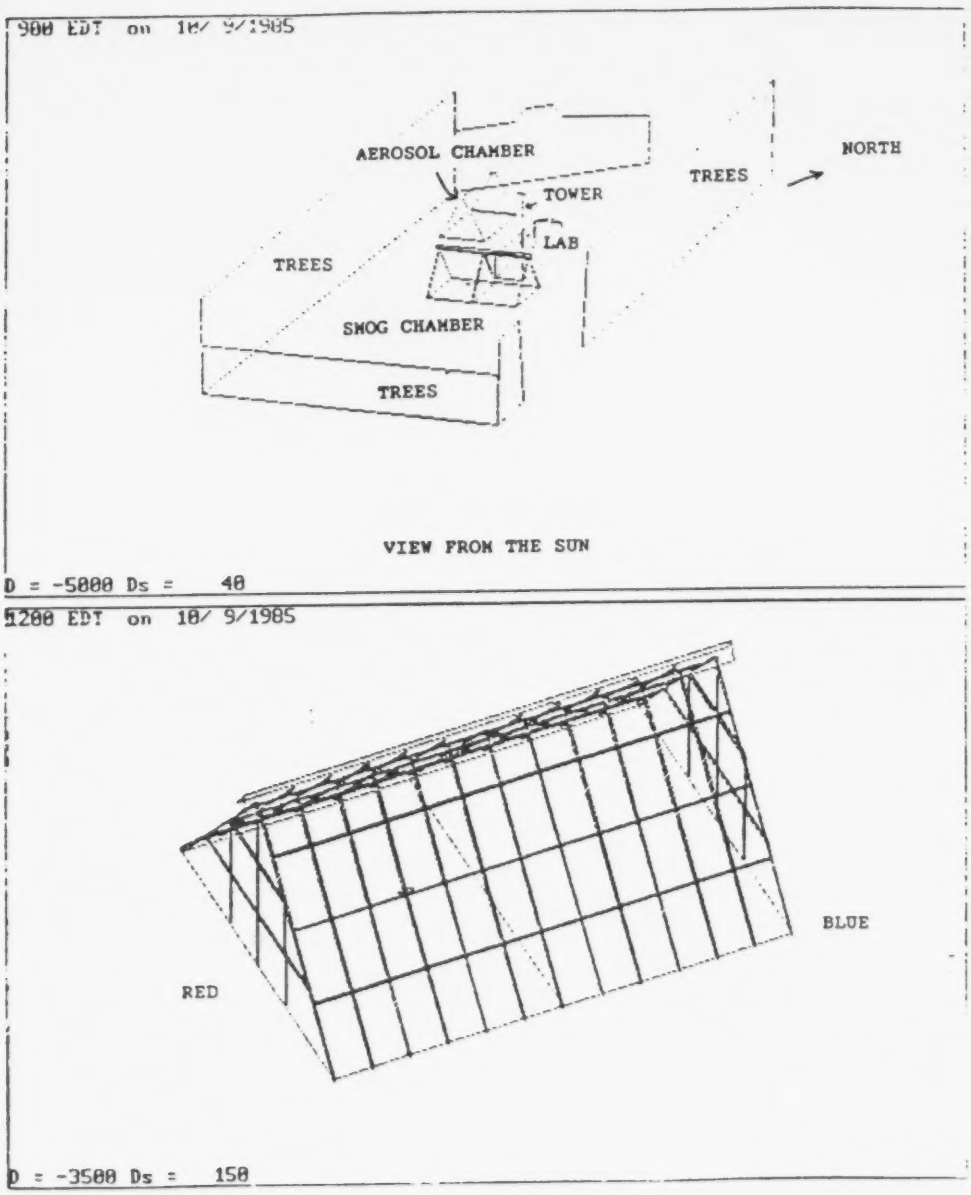

Figure 26. View of the Smog Chamber from the Sun Direction

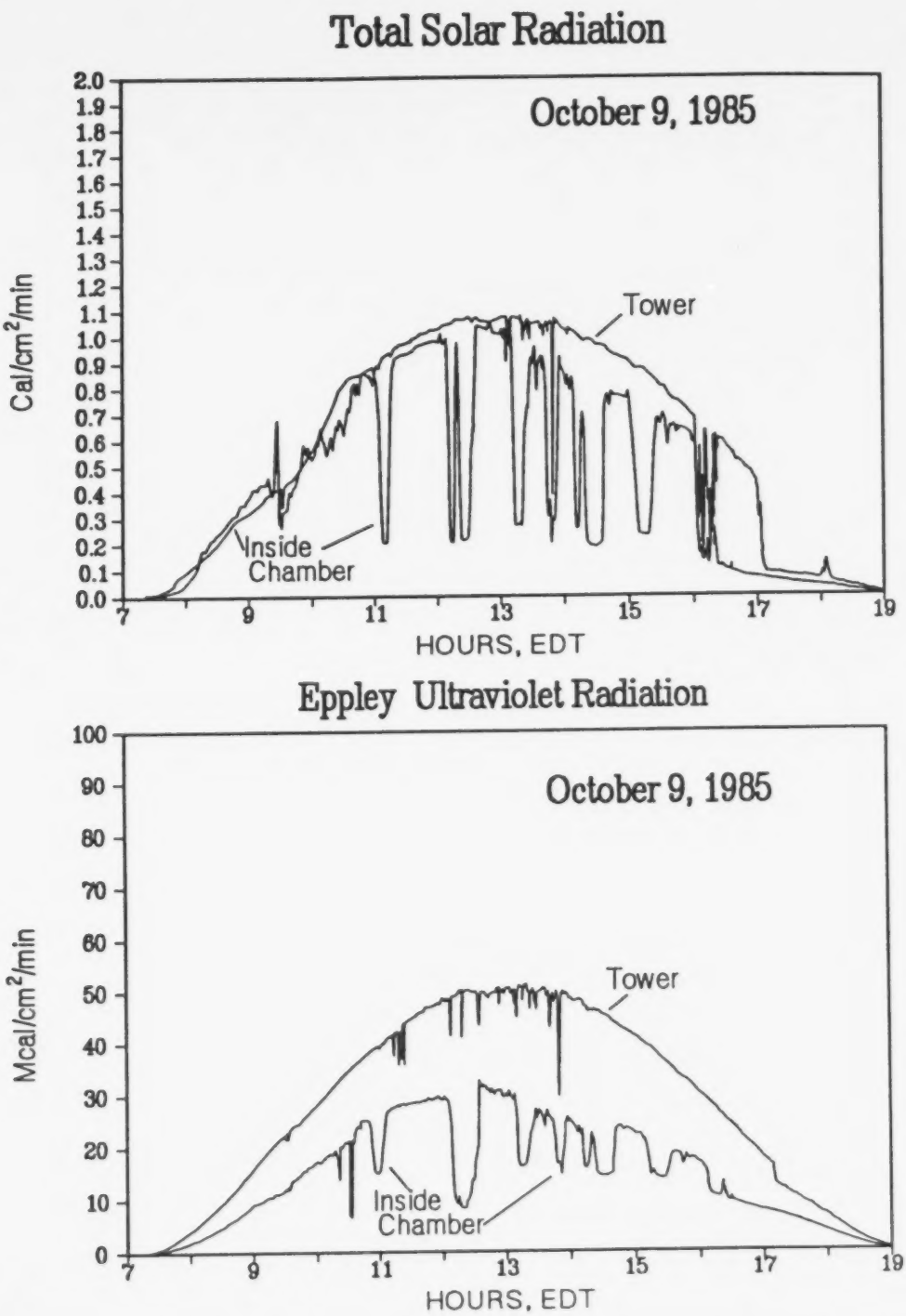

Figure 27. Inside and Outside Smog Chamber Light Measurements: TSR and UV.

attenuated just a few percent and the UV is attenutated about 35 to 40 percent. The inside measurements also show the dips caused by a shadow from the chamber rafter passing over the sensor as the sun moves.

There is much future work planned in this area of light measurement inside and outside the chamber. This includes measurements of light reflected from the chamber floor and within the shawdows of the rafters. Plans have been made to obtain an instrument which will allow high resolution spectra to be obtained from 300 to 900 nm, throughout the day, both inside and outside the chamber, looking up and down at the floor of the chamber.

Simulation of Continuous Emissions and Meteorological Dilution

Initial modeling of the dynamic experiments, where both continuous emissions and meteorological dilution were experimentally simulated in the smog chambers, was unsuccessful in simulating the dilution and injection tracers. This indicated that the rates, processes, or data, were not understood (or not ideal). Successful modeling of the tracers is necessary to determine and verify the rates and actual processes of both precursor injection, mixing, and dilution, and to obtain the best simulation results. Smog Chamber experiments were conducted to better understand these processes. The chamber was modified slightly to disperse the dilution air and the injected precursors. The resulting data indicated that this was not the problem. A hot-wire anemometer was used to "map" the air flow inside the chamber while the meteorological dilution was being simulated. The air appeared to be well mixed (it was thought that a dominant air pattern might cause channeling of the injected pollutants to the chamber exhaust door before complete mixing, resulting in excessive loss of precursors and non-ideal mixing).

Additional modeling and detailed analyses of the tracer data from the dynamic experiments conducted in the earlier research were performed to better understand these processes. The results showed that the small background levels of the tracers (in outside air) used are significant in experiments with large dilution and must be considered in the calculations of dilution and emissions rates from the tracer data taken during these experiments. When the background levels are considered and included in the dilution calculations, good agreement between simulation of the tracer profile and the experimental tracer data is obtained.

The actual dilution rate in each experiment was determinded by analysis of inert tracers injected into the chamber air before the experiment began. Carbon tetrachloride (CCl_4) and tetrachloroethylene (TCE) which elute rapidly on the

PAN analysis column of the electron capture detector gas chromatograph (ECD), were selected for the tracers. The sensitivity of the ECD for these compounds was such that a few parts per trillion (ppt) could be detected. Both compounds have low reactivity and only a few ppb of each tracer were injected. One difficulty with the CCl_4 tracers was that the ambient air at the research site had a 20-40 ppt background concentration of CCl_4. It was thus very important to account for the background contribution to the CCl_4 concentration in the chamber when large dilution had occurred and the chamber concentration had decreased to 30-50 ppt. Neglecting the background could cause a miscalculation of the dilution rate by as much as 50 percent in these cases.

The CCl_4 concentration profile for the large dilution side of June 27, 1983 is shown in Figure 28, along with the measured morning background that was extrapolated throughout the day. Although the chamber data appear to indicate an exponential decay (a least squares fit of an exponential function gave a rate of 3.1×10^{-3} min^{-1} with an $r^2 = 0.988$), analysis of the slope in each interval, corrected for the background entrainment, shows that the dilution rate was constantly changing (see Figure 29). These rate data show that the pressure balance between the chamber exhaust and the fan bypass required over two hours to reach an equilibrium value. That is, the chamber exhaust rate increased from zero to a nearly steady value over a two–hour period. The average value during the middle portion of the experiment was closer to 5×10^{-3} min^{-1}, a 60 percent larger value than the simple exponentially fitted rate. The fan was turned off at 1720 EDT and the dilution rate dropped to near zero.

Figure 30 shows the TCE tracer profile (solid line) resulting from injection of TCE from the CSTR at an exponentially decreasing rate and the large dilution that occurred in the June 27 experiment. The dotted line in Figure 30 was predicted by a model in which the exponential injection rate, kc, was calculated from the flow rate into and the volume of the CSTR and the dilution rates were calculated from the data plotted in Figure 28. The models prediction of the dilution data is also shown. The dilution rates applied to the prediction of the CSTR tracer show that there was nearly a perfect prediction of the behavior of the CSTR tracer (TCE). Therefore, in spite of the fact that ideal dilution profiles were not obtained by the bypass dilution system, careful analysis of tracer data produces an excellent description of the actual dilution in each experiment. The simulation results of both the static and dynamic sides of this experiment are shown in Figure 31.

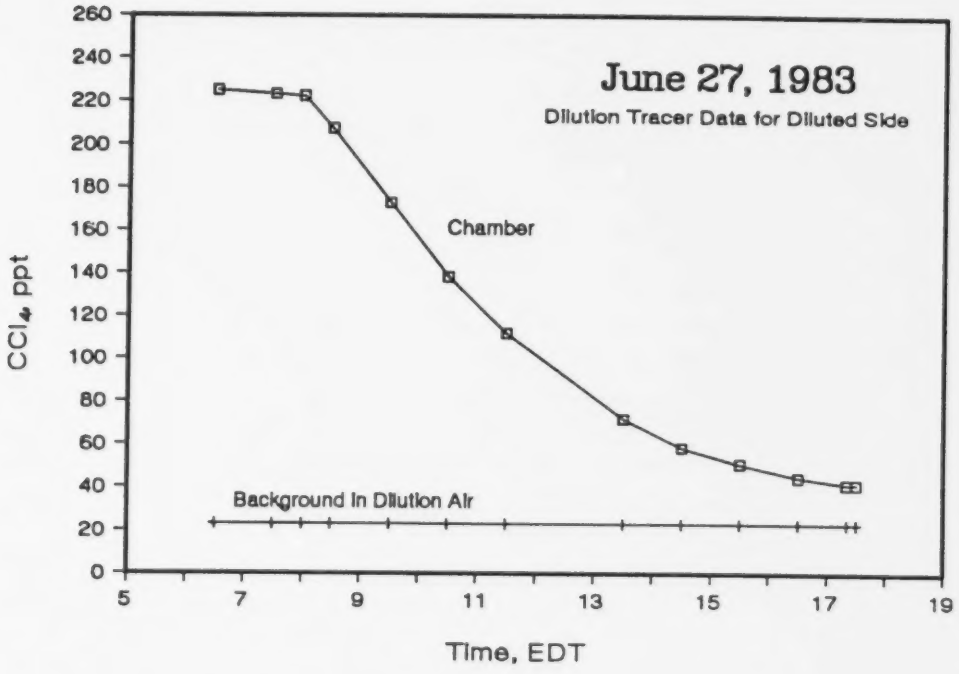

Figure 28. CCl_4 Dilution Tracer Data for Dynamic Side of June 27, 1983.

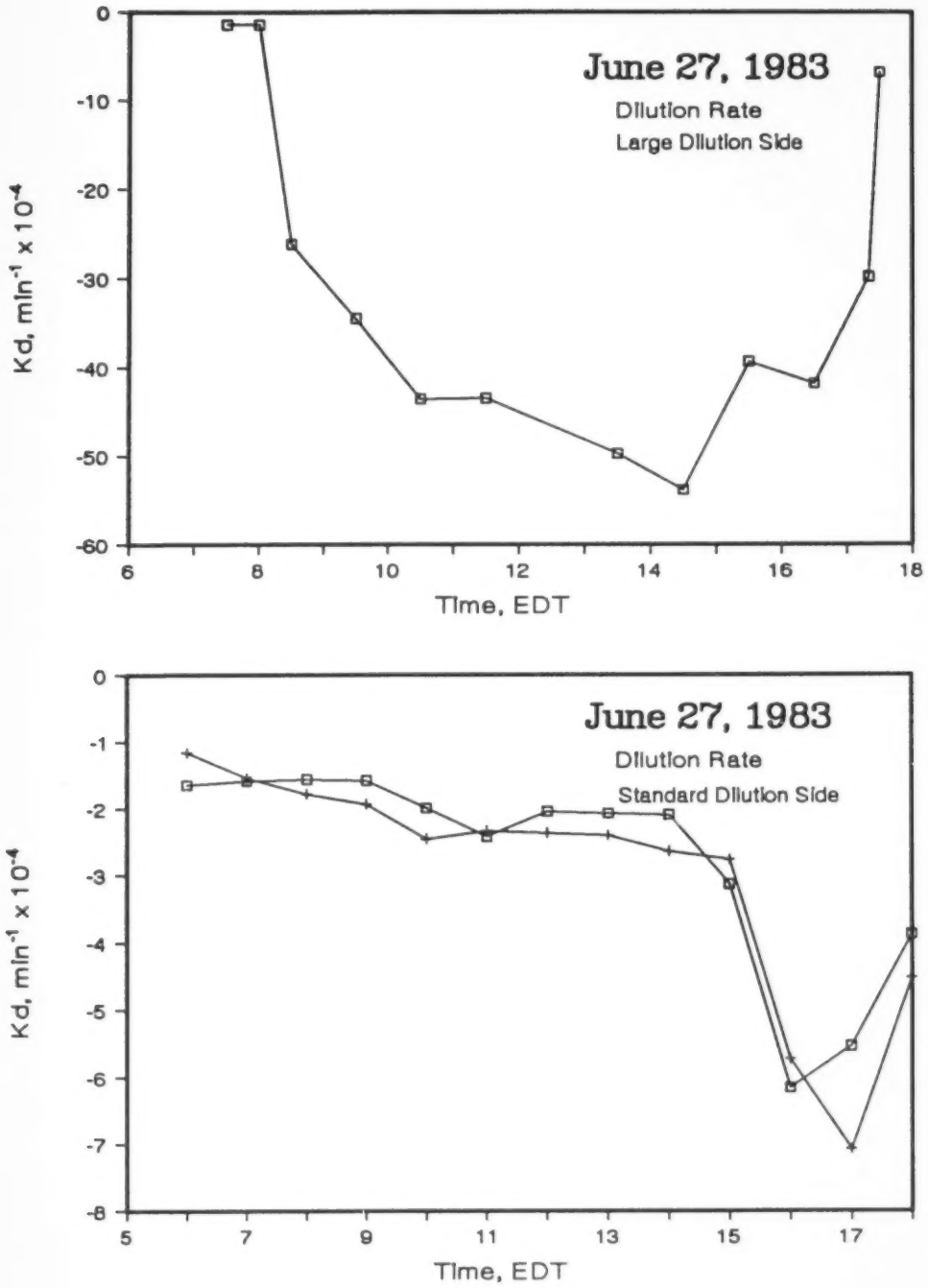

Figure 29. Calculated Dilution Rates for June 27, 1983.

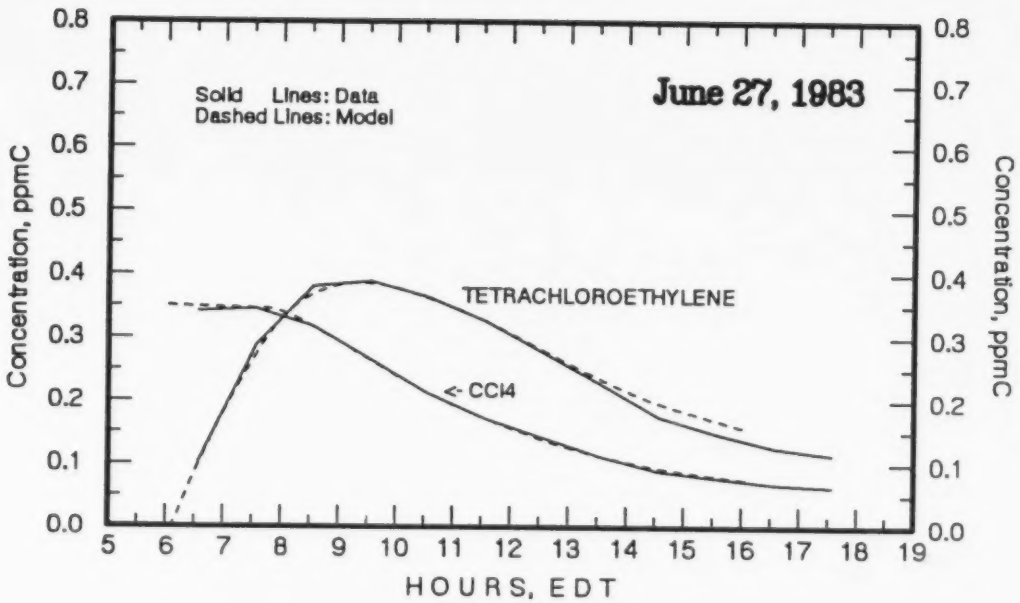

Figure 30. Modeled Injection and Dilution Rates for June 27, 1983.

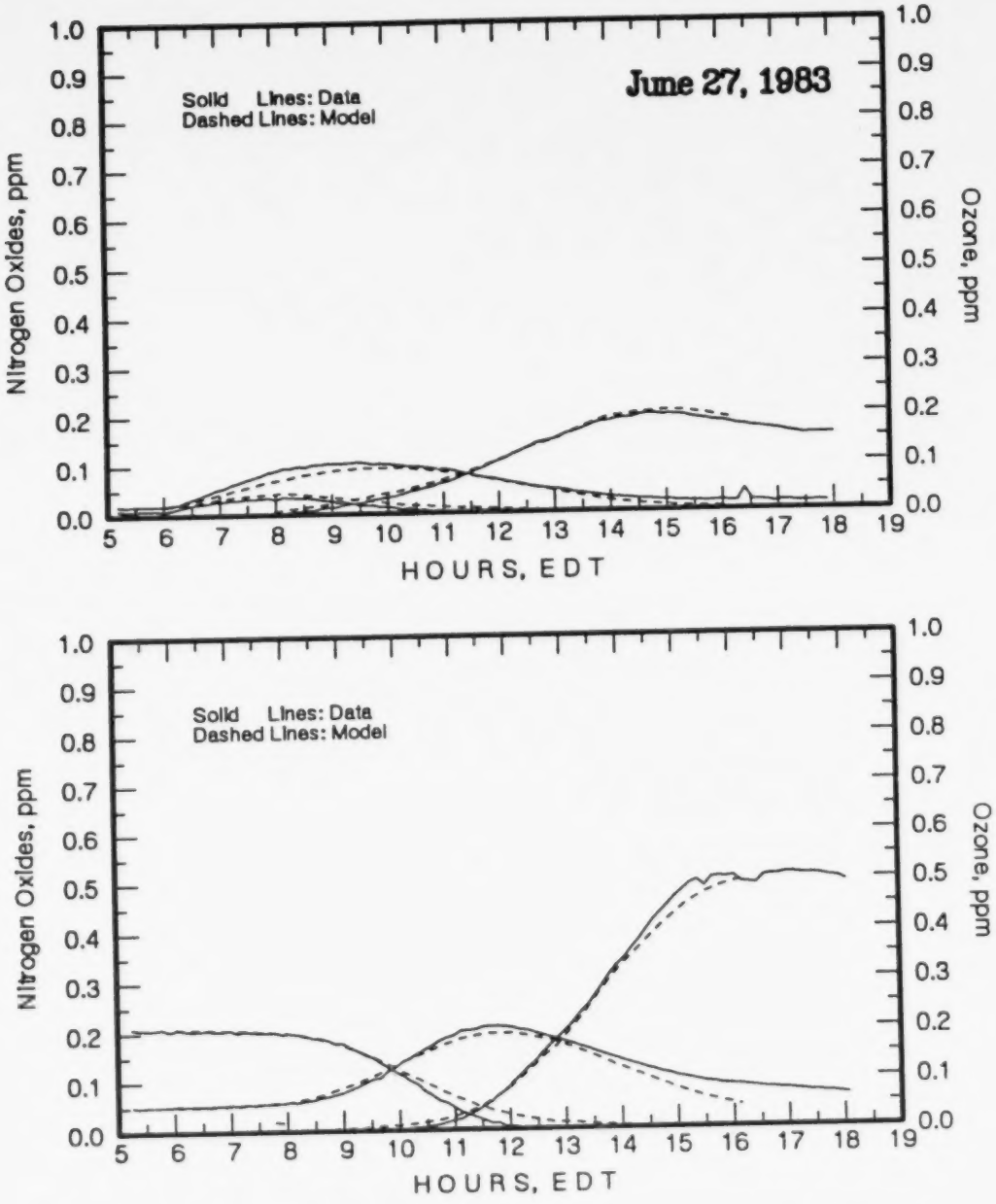

Figure 31. Dynamic Injection and Dilution vs. Standard Static Conditions.
Propylene, n-Butane, Toluene, NO_x; Matched Concentration If No Dilution;
CB4: Standard Model Conditions;
NO_x and O_3 Simulation Results;
Top: Continuous Injection and Dilution;
Bottom: Standard Static Conditions.

6

Database

Selecting Runs and Obtaining Data

These new experiments have been added to the original set of 346 experiments. The organization allows for easy identification and selection. Figure 32 and Figure 33 show the distribution of the experiments by series and HC Type. Model testing should proceed with the hierarchy described in the previous report. A database of the initial conditions and supporting information has been formed to select runs for a mechanism testing program. These new experiments fill-in a portion of a logical testing sequence which should provide useful tests of chemical mechanisms used to estimate hydrocarbon controls needed to meet the air quality standards for ozone.

Fully processed runs and the experimental conditions database are available on floppy diskettes. Copies other supporting information are available through the authors at a nominal cost. Contact Dr. Harvey E. Jeffries, Dept. of Environmental Sciences and Engineering, School of Public Health, Rosenau Hall, University of North Carolina, Chapel Hill, NC 27599.

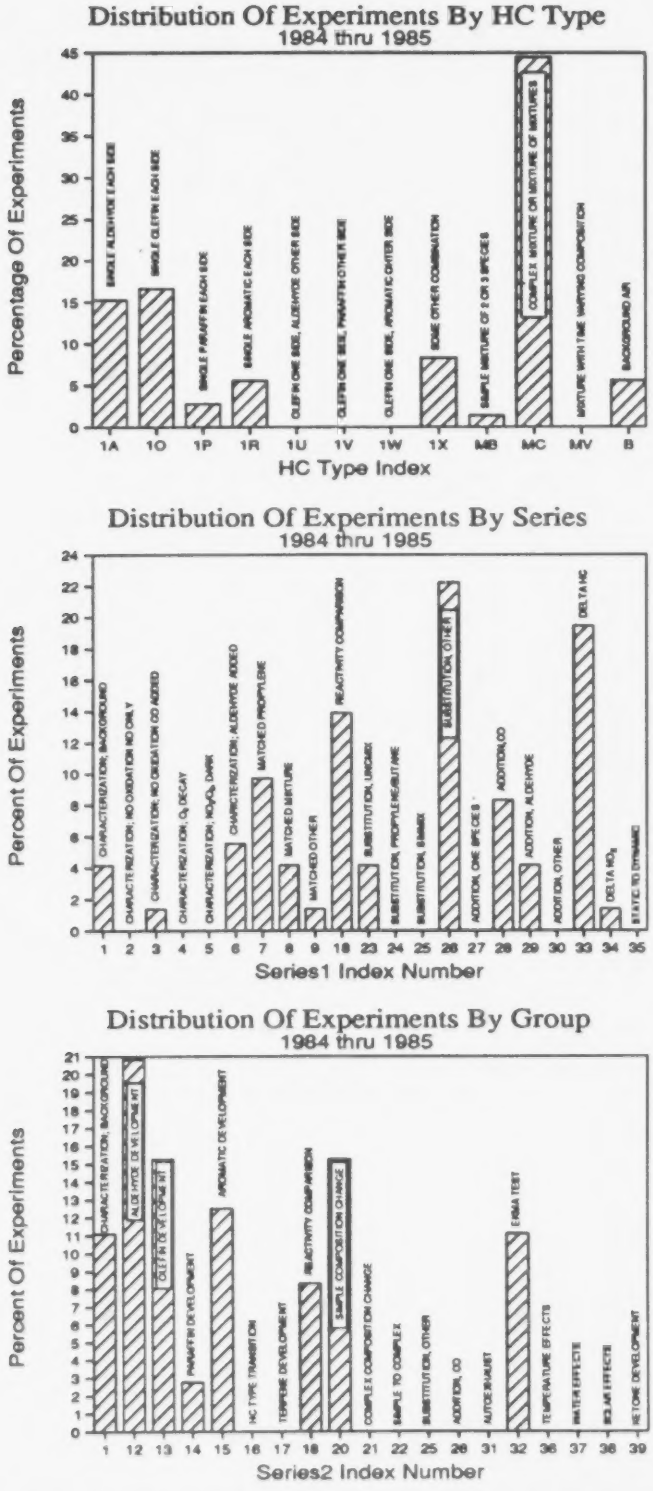

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Figure 32. Distribution of 1983-1985 Smog Chamber Experiments By Group And Hydrocarbon Type.

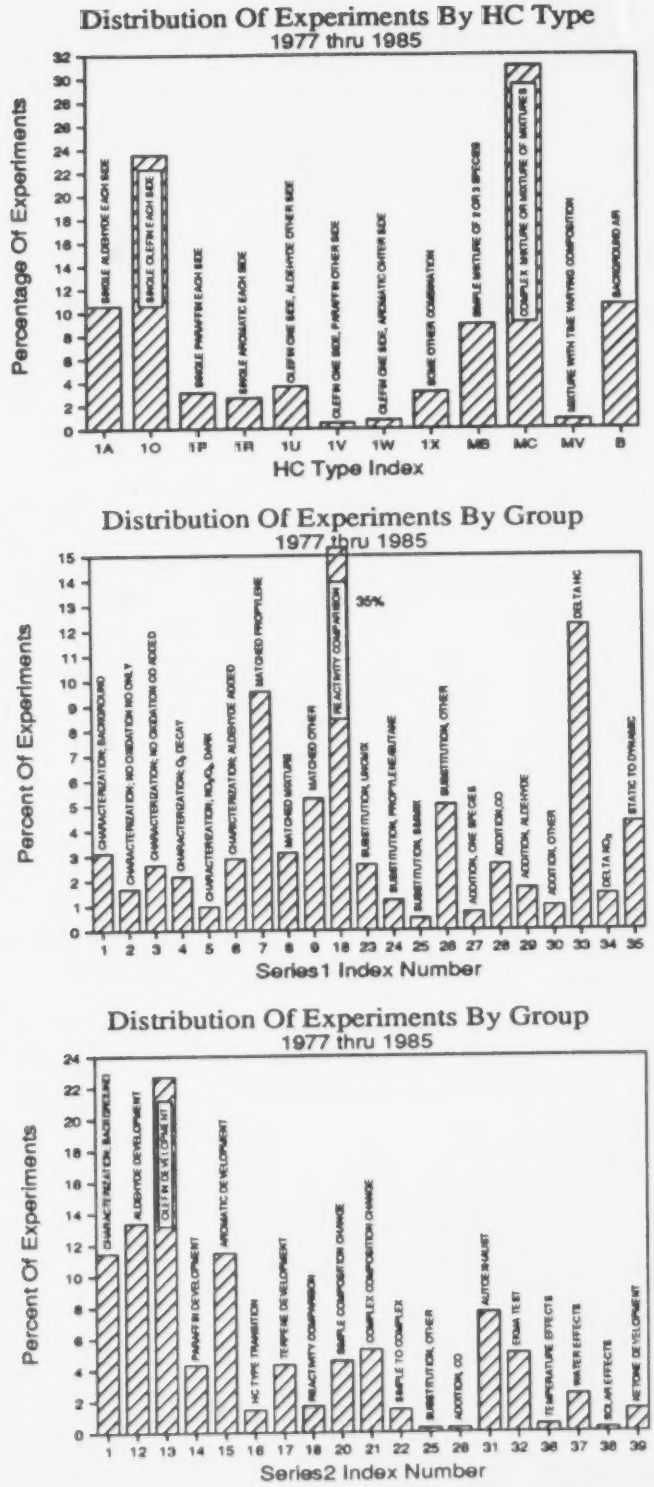

Figure 33. Distribution of 1977-1985 Smog Chamber Experiments By Group And Hydrocarbon Type.

References

1 Jeffries H.E., Sexton K.G., Kamens R.M., Holleman M.S, "Outdoor Smog Chamber Experiments To Test Photochemical Models: Phase II", Final Report (EPA/600/3-85/029), Environmental Protection Agency, Research Triangle Park, N.C., March 1985; NTIS No. PB 85-191 542/AS.

2 Sexton K.G., Jeffries H.E., Arnold, J.R.,Kale T.L., Kamens R.M., "Validation Data for Photochemical Mechanisms ", Final Report (EPA/600/3-87/003), Environmental Protection Agency, Research Triangle Park, N.C., April 1987; NTIS No. PB 87-145 298/AS.

3 Jeffries H.E., Sexton K.G., Morris, T.P., Jackson M., Goodman R.G., Kamens R.M., Holleman M.S, "Outdoor Smog Chamber Experiments Using Automobile Exhaust", Final Report (EPA/600/S-85/032), Environmental Protection Agency, Research Triangle Park, N.C., June 1985; NTIS No. PB 85-191 708/AS.

4 Kopczynski S. *et al.*, "Photochemistry of Atmospheric Samples in Los Angeles," *Enviro. Sci. Technol.*, **6**, 342, 1972.

5 Killus J., Whitten G., "Technical Discussion Relating to the Use of the Carbon Bond Mechanism in OZIPM/EKMA," EPA-450/4-84-009, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1984.

6 Gipson G., Freas W., "An Analysis of Organic Species Data Collected in the Northeast Corridor Regional Modeling Project," U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, presented at 77th APCA meeting, San Francisco, CA, 1984.

7 Schiff, H.K., Hastie, D.R., Mackay, G.I., Iguchi, T., Ridley, B.A., "Tunable Diode Laser Systems For Measuring Trace Gases In Tropospheric Air", Environ. Sci. Tech., V17, pp 352A-364A, 1983 .